PB-227 756

ANALYTICAL REFERENCE SERVICE TRAINING PROGRAM. SAMPLE TYPE III-B, WATER, FLUORIDE

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

August 1961

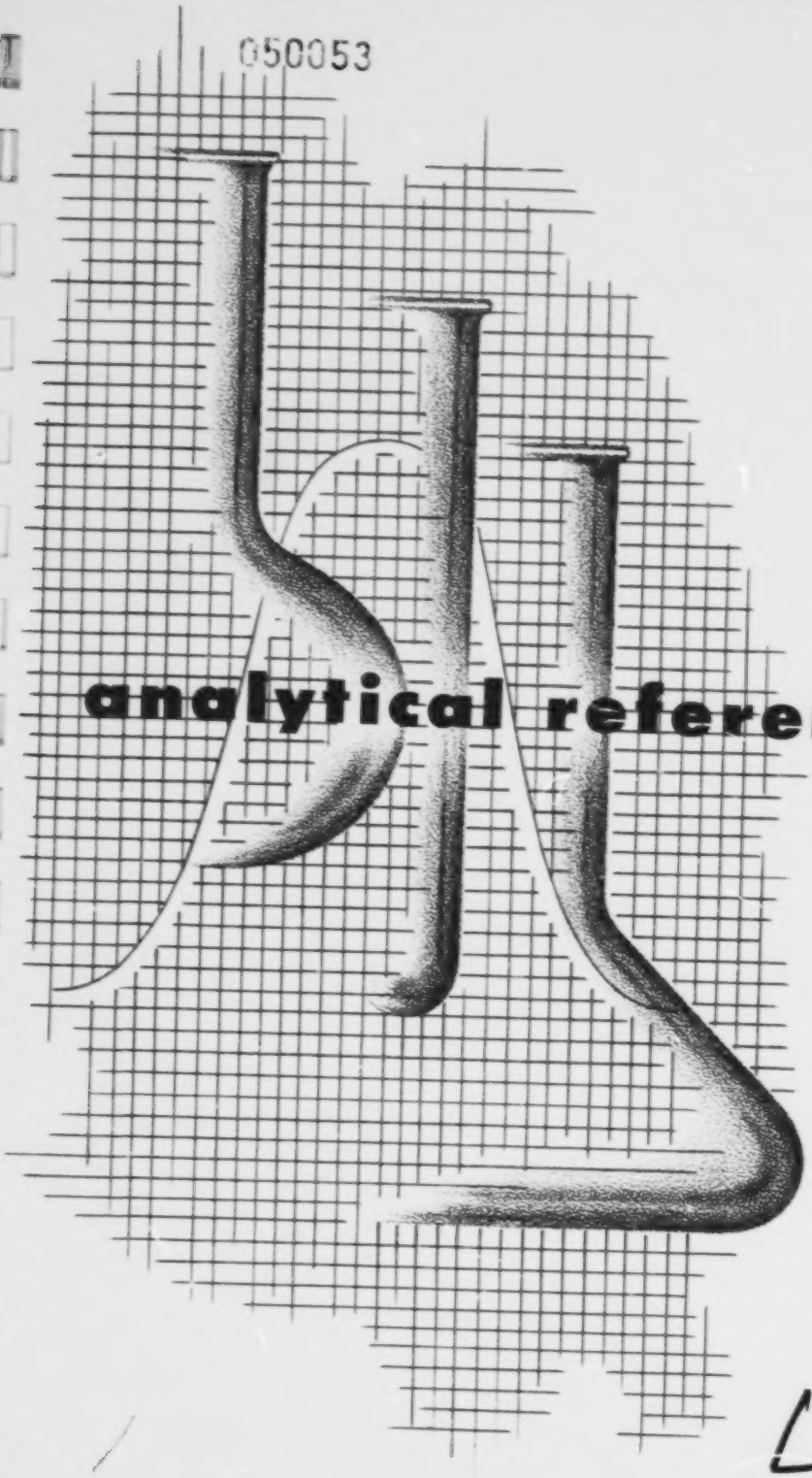
DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

050053

PB 227 756



SAMPLE TYPE III-B
WATER, FLUORIDE
AUGUST, 1961

analytical reference service

TRAINING PROGRAM

Robert A. Taft

SANITARY ENGINEERING CENTER

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
CINCINNATI, OHIO

Reproduced by
NATIONAL TECHNICAL INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

94

ANALYTICAL REFERENCE SERVICE

SAMPLE TYPE III-B (WATER, FLUORIDE)

Report of a laboratory performance study conducted jointly with the participating member organizations.

Prepared by the

Analytical Reference Service

TRAINING PROGRAM

U. S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
Public Health Service
Bureau of State Services
Division of Engineering Services

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1961

ANALYTICAL REFERENCE SERVICE

STAFF

F. S. Kelso, In Charge
R. J. Lishka, Chemist
M. C. Blum, Chemist
D. K. Malott, Physical Science Aide
M. K. Thomas, Physical Science Aide
C. S. Sayers, Secretary

CONTENTS

FOREWORD	iv
ANALYTICAL REFERENCE SERVICE MEMBERS	vi
PARTICIPANTS IN THIS STUDY	ix
COMPLETED REPORTS	x
BACKGROUND INFORMATION	1
PURPOSE OF STUDY	1
PREPARATION OF SAMPLE	2
TREATMENT OF DATA	3
LABORATORY METHODS	3
DISCUSSION OF RESULTS AND STATISTICAL SUMMARY	4
SUMMARY OF COMMENTS - DISTILLATION PROCEDURES	10
COMMENTS ON DISTILLATION PROCEDURES	11
SUMMARY OF COMMENTS - SPADNS PROCEDURE	21
COMMENTS ON SPADNS PROCEDURE	22
SUMMARY OF THE REPORT	37
COMPARISON OF REPLICATE VALUES	38
SUMMARY OF ARITHMETIC MEANS	74
APPENDIX - Bar Graphs	76

Solution A Undistilled
Solution A Distilled
Solution B Undistilled
Solution B Distilled
Solution C Undistilled
Solution C Distilled

FOREWORD

The Analytical Reference Service is a voluntary association of organizations responsible for the conduct of laboratory programs. It is conducted by the Training Program of the Robert A. Taft Sanitary Engineering Center for the evaluation of laboratory methods in the field of sanitary engineering. Evaluations are obtained by the cooperative efforts of the member organizations in analysis of identical samples. This cooperative mechanism provides:

1. Statistical evaluation of procedures, including precision and accuracy.

2. Opportunity for comparison of laboratory procedures and results between laboratories having similar responsibilities.

3. Exchange of information regarding weaknesses of currently approved methods.

4. Evidence of the need for further development of methods or for entirely new approaches.

5. A framework of broad-scale evaluation of new analytical methods.

Initially the program was directed toward examination of water. It has been broadened to include other types of examinations and other media.

In the conduct of these studies, samples are designed and prepared containing measured amounts of the desired constituents. Decisions as to qualitative makeup are made by the staff of ARS, the membership, and consultants in the field of analytical methodology. Notice of a particular study together with the qualitative makeup of the sample and the availability is forwarded to all member organizations.

Foreword

Immediately on receipt of the indication of willingness to participate, a portion of the sample is shipped with accompanying data forms which provide space for numerical values and a narrative critique of the analytical procedures used. The laboratories of the agencies are urged to comment on the methods, including difficulties, modifications, sources of error, and other factors. Results are requested usually within sixty days.

These results, including the comments, are compiled as in the accompanying report. This report is based upon the information supplied by the participants in this study. In the Water-Fluorides, Type III study prepared in 1958, 27 agencies participated. Our experience in the past indicates that when a study is repeated, there is a large increase in the number of participants. In this second fluoride study 50 agencies cooperated.

Reports upon a Water-Minerals study and and Air-Lead study are being compiled by the ARS staff. A Water-Metals study is now in progress, with some 80 members assisting. Member agencies are currently returning questionnaires indicating their choices for future studies.

Our membership now consists of 115 agencies with many diversified interests. The very significant increase in membership being experienced is a strong indication of the broad interest in and need for this type of service.

H P Kramer

H. P. Kramer
Chief, Training Program

ANALYTICAL REFERENCE SERVICE MEMBERS*

STATE AGENCIES

Alabama Water Improvement Commission
Arizona State Department of Health
Arkansas State Board of Health
California State Department of Public Health (Berkeley)
California State Department of Public Health (Los Angeles)
California Department of Water Resources
Colorado State Department of Public Health
Connecticut State Department of Health
Florida State Board of Health (Bureau of Laboratories, Jacksonville)
Florida State Board of Health (Sanitary Engineering, Jacksonville)
Florida State Board of Health (Pensacola)
Florida State Board of Health (Winter Haven)
State of Hawaii Department of Health
Idaho Department of Health
Illinois State Department of Public Health (Chicago)
Illinois State Department of Public Health (Springfield)
Illinois State Water Survey Division
Indiana State Board of Health
Kansas State Board of Health (Sanitary Engineering Laboratories)
Kentucky State Department of Health
Louisiana State Board of Health
Maryland State Department of Health
Maryland State Water Pollution Control Commission
Massachusetts Department of Public Health
Michigan State Department of Health
Michigan Water Resources Commission
Minnesota State Department of Health
Missouri Department of Public Health & Welfare
Montana State Board of Health
Nebraska State Department of Health
Nevada State Department of Health (Las Vegas)
Nevada State Department of Health (Reno)
New Hampshire Water Pollution Commission
New Jersey Department of Health
New Mexico State Department of Public Health
New York State Department of Health
New York State Conservation Department
North Carolina Department of Water Resources

*July, 1961

Ohio State Department of Health
Oklahoma State Department of Health
Oregon State Board of Health
Pennsylvania Department of Health
Rhode Island Department of Health
South Carolina Water Pollution Control Authority
South Dakota Department of Health
Tennessee Stream Pollution Control Board
Texas State Department of Health
Utah State Department of Health
Vermont State Department of Health
Vermont State Water Conservation Board
Virginia State Department of Health
Virginia State Water Control Board
Washington State Department of Health
West Virginia State Water Resources Commission
Wisconsin State Board of Health

MUNICIPAL AGENCIES

Metropolitan Water District of Southern California
Los Angeles Department of Water and Power
Los Angeles County Flood Control District
Los Angeles Department of Public Works (Hyperion Treatment Plant)
City of Pasadena
Chicago Department of Water and Sewers
Topeka, Kansas Water Works
Flint Water Plant, Department of Public Works and Utilities
St. Louis County Water Company
St. Louis Department of Health and Hospitals
Metropolitan Utilities District (Omaha, Nebraska)
City of Durham Department of Water Resources (North Carolina)
Dayton Department of Service and Buildings
Philadelphia Suburban Water Company
Philadelphia Water Quality Control and Research Division

FEDERAL AGENCIES

Food and Drug Administration, Division of Pharmacology, Washington, D. C.
Tennessee Valley Authority, Wilson Dam, Alabama (Occupational Health Branch)
Tennessee Valley Authority, Chattanooga, Tennessee (Stream Pollution Control)
2794th U. S. Air Force Dispensary - Class B
U. S. Army Environmental Hygiene Agency, Maryland

U.S. Dept. of the Interior, Geological Survey, Sacramento, California
U.S. Dept. of the Interior, Geological Survey, Denver, Colorado
U.S. Dept. of the Interior, Bureau of Reclamation, Denver, Colorado
U.S. Dept. of the Interior, Geological Survey, Columbus, Ohio
U.S. Dept. of the Interior, Geological Survey, Philadelphia, Pennsylvania
Pearl Harbor Naval Shipyard

UNIVERSITIES

Case Institute of Technology, Dept. of Civil and Sanitary Engineering
Columbia University
Georgia Institute of Technology, Dept. of Applied Biology
University of Pittsburgh, Graduate School of Public Health
Purdue University, Department of Chemistry
Rutgers University, Department of Sanitation

INDUSTRY

American Cyanamid Company, Bound Brook, New Jersey
Atlantic Refining Company, Philadelphia, Pennsylvania
Battelle Memorial Institute, Columbus, Ohio
California Water Service Company, San Jose, California
Central Farmers Fertilizer Company, Montpelier, Idaho
Culligan, Inc., Northbrook, Illinois
Dearborn Chemical Company, Chicago, Illinois
E.I. du Pont de Nemours & Co., Aiken, South Carolina
Ekroth Laboratories, Inc., Brooklyn, New York
Food Machinery & Chemical Corp., Pocatello, Idaho
Goodyear Atomic Corporation, Portsmouth, Ohio
Industrial Chemicals, Inc., South Bend, Indiana
Ionics, Incorporated, Cambridge, Massachusetts
Hagan Chemicals & Controls, Inc., Pittsburgh, Pennsylvania
Kennecott Copper Corporation, Salt Lake City, Utah
Monsanto Chemical Company, St. Louis, Missouri
NALCO Chemical Company, Chicago, Illinois
Radiation Detection Company, Palo Alto, California
Reynolds Electrical & Engineering Company, Las Vegas, Nevada
Roy F. Weston, Inc., Newtown Square, Pennsylvania
Sandia Corporation, Sandia Base, Albuquerque, New Mexico
Tracerlab, Inc., Richmond, California

FOREIGN

Vancouver, B.C., Department of National Health & Welfare
Ottawa, Ontario, Department of National Health & Welfare
Ottawa, Ontario, Occupational Health Division, Department of National Health & Welfare

PARTICIPANTS IN THIS STUDY

Arizona State Department of Health
California State Department of Public Health (Los Angeles)
California Department of Water Resources
Connecticut State Department of Health
Florida State Board of Health (Bureau of Laboratories, Jacksonville)
Idaho Department of Health
Illinois State Water Survey Division
Kentucky State Department of Health
Maryland State Department of Health
Michigan State Department of Health
Minnesota State Department of Health
Missouri Department of Public Health & Welfare
Montana State Board of Health
Nebraska State Department of Health
New Jersey Department of Health
New Mexico State Department of Public Health (Contract Lab)
New York State Department of Health
North Carolina Department of Water Resources
Ohio State Department of Health
Oregon State Board of Health
Pennsylvania Department of Health
Rhode Island Department of Health
Tennessee Stream Pollution Control Board
Texas State Department of Health
Utah State Department of Health
Vermont State Department of Health
Virginia State Department of Health
Washington State Department of Health
West Virginia State Water Resources Commission
Metropolitan Water District of Southern California
Los Angeles Department of Water and Power
Chicago Department of Water and Sewers
Flint Water Plant, Department of Public Works and Utilities
St. Louis County Water Company
Philadelphia Water Quality Control and Research Division (Contract Lab)

Tennessee Valley Authority, Wilson Dam, Alabama (Occupational Health Branch)
Tennessee Valley Authority, Chattanooga, Tennessee
U.S. Army Environmental Hygiene Agency, Maryland
U.S. Dept. of the Interior, Geological Survey, Sacramento, California
U.S. Dept. of the Interior, Bureau of Reclamation, Denver, Colorado
U.S. Dept. of the Interior, Geological Survey, Columbus, Ohio
Case Institute of Technology, Dept. of Civil and Sanitary Engineering
University of Pittsburgh, Graduate School of Public Health
California Water Service Company, San Jose, California
Central Farmers Fertilizer Company, Montpelier, Idaho
Dearborn Chemical Company, Chicago, Illinois
Food Machinery & Chemical Corp., Pocatello, Idaho
Goodyear Atomic Corporation, Portsmouth, Ohio
Vancouver, B.C., Department of National Health & Welfare
Ottawa, Ontario, Department of National Health & Welfare

SAMPLES ON WHICH REPORTS HAVE BEEN COMPLETED

SAMPLE TYPE I AND I-A

(Water, Minerals) analyzed for calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium and potassium.

SAMPLE TYPE II

(Water, Heavy Metals) analyzed for copper, cadmium, aluminum, chromium, iron, manganese, and zinc.

SAMPLF TYPE III

(Water, Fluoride) analyzed for fluoride in the presence and absence of interferences with and without distillation, using a specified procedure.

SAMPLE TYPE IV

(Air, Inorganics) analyzed for chloride, sulfate, fluoride and nitrate in aqueous solution and on glass fiber hi-vol filter mats.

SAMPLE TYPE V

(Water, Radiological) analyzed for gross beta activity.

SAMPLE TYPE V-B

(Water, Radiological) analyzed for gross beta and gamma activity.

SAMPLE TYPE VI

(Water, Surfactant) analyzed for surfactant in various waters.

SAMPLE TYPE VII

(Water, Oxygen Demand) analyzed for biochemical oxygen demand and chemical oxygen demand.

SAMPLES NOW UNDER STUDY

(Water, Minerals, No. 3) analyzed for calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium and potassium.

(Air, Lead, No. 1) analyzed for lead.

(Water, Metals, No. 2) to be analyzed for copper, cadmium, aluminum, chromium, iron, manganese, zinc, and lead.

SAMPLE TYPE III-B (WATER, FLUORIDE)

BACKGROUND INFORMATION

At the present time, approximately 1968 communities serving 38.5 million people in the United States are fluoridating their water supplies. Since strict control of the concentration of fluoride is required, fluoride determinations of raw and finished water have become routine in many laboratories.

Most of the fluoride methods in current use are sensitive to interferences commonly encountered in surface waters. Distillation is therefore required as a preliminary step in the determination. In a previous Analytical Reference Service study, it was found that the traditional Willard & Winter distillation procedure, while effective in removal of interferences, significantly reduced the precision of the determination. Recently Bellack [1] has developed a simplified distillation method which is claimed to be as effective as the older procedures but requires less elaborate glassware and less operator attention.

The same group of investigators have reported on an analytical procedure[2] utilizing sodium 2-(p-Sulfophenylazo)-1, 8-dihydroxynaphthalene-3, 6- disulfonate (more conveniently designated as SPADNS), which has certain advantages over current methods. This method and the Bellack distillation method have been included as tentative procedures in the eleventh edition of Standard Methods for the Examination of Water, Sewage, and Industrial Wastes.

PURPOSE OF THIS STUDY

In the study reported here, the sample was designed to test the effectiveness of the Bellack distillation procedure and to evaluate the SPADNS method for the determination of fluoride in water, when compared to other more routine analytical methods.

---

(1) Bellack, Ervin J., "Simplified Fluoride Distillation Method", Journal American Water Works Association 50:4, pp. 530-36, 1958.

(2) Bellack, Ervin J., and Schouboe, P. J., "Rapid Photometric Determination of Fluoride in Water", Analytical Chemistry 30:2032, 1958.

PREPARATION OF SAMPLE

Substrate:

Deionized distilled water

Chemicals:

ACS Reagent Grade from freshly opened bottles

Composition:

A family of three separate solutions designated A, B, and C as follows:

Constituent	Solution A mg/l	Solution B mg/l	Solution C mg/l
Fluoride	0.83	0.57	0.68
Alkalinity	0.	300.	300.
Sulfate	0.	200.	200.
Aluminum	0.	10.	2.
Hexametaphosphate	0.	0.	2.5

Solution A served as a control since no interfering substances were added. Unsatisfactory results obtained with Solution A would indicate inadequate methods or faulty technique. Comparison of the values reported on Solution A undistilled and distilled demonstrates the degree of recovery of fluoride by the Bellack distillation.

Solution B contained sulfate and aluminum as interferences. These were investigated because of the frequency of their appearance in water supplies and because the SPADNS method employs a relatively simple procedure for eliminating errors due to aluminum and is reported to be very tolerant of sulfate. The resulting data should measure the effectiveness of the SPADNS correction procedure and illustrate the influence of these interferences on other analytical methods.

Solution C contained hexametaphosphate as an additional interference, as it is a serious source of error in all fluoride methods. Distillation is the recommended method for removing phosphate interference. Data on Solution C should indicate the effect of hexametaphosphate on the analytical methods used, as well as the effectiveness of the Bellack distillation in removing phosphate interference.

Distillation was requested for all solutions because it is the recommended method for eliminating sulfate and aluminum. Both Solutions B and C contained 300 mg/l of alkalinity, added as sodium bicarbonate, so that the solutions would more nearly duplicate natural samples. No provision was made for evaluation of the alkalinity as an interfering material.

TREATMENT OF DATA

It was requested that all results be reported to the second decimal, a common practice in photometric procedures. For the visual methods, however, the second decimal becomes a subjective number. In tabulating the results where the second digit was not included, this digit was assumed to be zero; for example, a result reported as 0.9 is listed as 0.90.

In this study, 53 laboratories performed 300 distillations and reported 1797 analytical results. Such an abundance of data could lend itself to intensive statistical treatment but for this report only the common statistical measures are used.

The standard deviation in the raw data was calculated by using the difference between the reported values and the amount of fluoride actually added. All reported values greater than two standard deviations were then rejected, and the standard deviation was recalculated. This refined standard deviation reflects the accuracy of the analytical methods employed in this study, since approximately 95 per cent of the reported values are retained.

Authorities in the field of fluoridation have generally agreed that an acceptable fluoride method should be capable of producing an accuracy of $\pm$ 0.10 mg/l at a concentration level of approximately 1.0 mg/l. This measure of accuracy is used in this report as a standard of performance.

LABORATORY METHODS

Since most of the 53 laboratories participating in this study analyze fluoride samples routinely, the data obtained are based on work by analysts familiar with one or more fluoride methods. The routine methods specified by the participants for the comparative analyses were as follows:

Method	Users
Scott-Sanchis	20
Megregian-Maier	17
ECR	4
Other	8
No comparison performed	4

DISCUSSION OF RESULTS

Solution A (0.83 mg/l F)

On Solution A, which contained no interferences, a majority of the laboratories reported satisfactory results on the undistilled aliquots. Using the SPADNS procedure, 46 laboratories obtained results within ± 0.10 mg/l of the true value. Using comparative methods, 43 laboratories obtained results within ± 0.10 mg/l. The arithmetic mean of all SPADNS values without distillation was 0.84 mg/l, as compared to 0.84 mg/l for the Mergregian-Maier, 0.80 mg/l for the Scott-Sanchis, 0.85 mg/l for the ECR, and 0.85 mg/l for the remaining procedures. These data indicate that, in the absence of interfering substances, the average laboratory can routinely produce results within the ± 0.10 mg/l limit, employing either the SPADNS or other commonly used methods.

When Solution A was distilled, the results again were satisfactory, although the standard deviation was increased. Of the 53 laboratories submitting results on the SPADNS procedure, 38 obtained values within ± 0.10 mg/l of the true value. Using other methods, again 43 values were within this range. The arithmetic mean of all the SPADNS values with distillation was 0.81 mg/l, as compared to 0.79 for the Megregian-Maier, 0.81 mg/l for the Scott-Sanchis, 0.84 mg/l for the ECR, and 0.82 mg/l for the other methods.

From the data on Solution A the following conclusions may be drawn:

1. Using either the SPADNS or other routine methods, fluoride can be measured in the absence of interfering substances to within ± 0.10 mg/l at the 1.0 mg/l level.

2. In common with other distillation procedures, the Bellack distillation constitutes a potential source of error in fluoride measurement, as shown by the increased standard deviation.

Statistical Summary, Solution A (0.83 mg/l)

Method	Undistilled					Distilled				
	No. of Analyses	Arith. Mean	Median	Range	Std. Dev.	No. of Analyses	Arith. Mean	Median	Range	Std. Dev.
SPADNS	53	0.84	0.83	0.63-1.34	0.067	53	0.81	0.82	0.25-1.14	0.089
M & M	17	0.84	0.82	0.65-0.99	0.033	16	0.79	0.82	0.42-0.91	0.073
S & S	20	0.80	0.80	0.63-0.88	0.039	20	0.81	0.80	0.63-0.90	0.052
ECR	4	0.85	0.83	0.80-0.92	0.047	4	0.84	0.82	0.79-0.91	0.045
Other	8	0.85	0.80	0.76-1.00	0.091	7	0.82	0.79	0.73-1.00	0.054

Solution B (0.57 mg/l F, 200 mg/l SO_4, 10.0 mg/l Al)

Solution B contained two interferences, sulfate at the concentration of 200 mg/l and aluminum at a concentration of 10.0 mg/l. The SPADNS procedure proposes to correct for these interferences without distillation. Where aluminum is present in the sample, it is necessary to make an additional absorbance reading after 15 minutes. An appreciable drop in absorbance indicates interference from the aluminum ion. A 2-hour wait before reading will eliminate interference from 3 ppm Al. A 4-hour wait will eliminate interference from 30 ppm Al. The arithmetic mean of all SPADNS values without distillation was 0.61 mg/l, with 38 groups reporting values within the desired limits.

For the undistilled solution, the arithmetic mean was 0.34 mg/l for M & M, 0.40 mg/l for S & S, 0.64 mg/l for ECR, and 0.53 mg/l for other methods. Of the 48 laboratories reporting a comparative analysis, only 14 values were within $\pm$ 0.10 mg/l of the true value. As shown in the bar charts, nearly all the comparative procedures yielded very low values while the SPADNS method yielded a normal distribution and a standard deviation within the accepted limits. It is apparent that the SPADNS method effectively removed the aluminum interference without the necessity of distillation.

With the distilled solution, the SPADNS results showed no significant change but, in most of the other methods, the improvement was dramatic. The SPADNS data have an arithmetic mean of 0.60 mg/l, the M & M of 0.57 mg/l, the S & S of 0.57 mg/l, the ECR of 0.55 mg/l, and the other procedures of 0.63 mg/l.

The data on Solution B indicate that:

1. When aluminum and sulfate are the only interferences in the sample the SPADNS method is advantageous when distillation is not performed.

2. Distillation for removal of sulfate and aluminum interferences is advisable when either the Scott-Sanchis or Megregian-Maier procedure is used.

Statistical Summary, Solution B (0.57 mg/l)

Method	Undistilled					Distilled				
	No. of Analyses	Arith. Mean	Median	Range	Std. Dev.	No. of Analyses	Arith. Mean	Median	Range	Std. Dev.
SPADNS	53	0.61	0.60	0.29-1.04	0.099	53	0.60	0.59	0.00-1.09	0.103
M & M	17	0.34	0.34	0.09-0.65	0.257	16	0.57	0.56	0.31-0.77	0.098
S & S	20	0.40	0.40	0.21-0.60	0.207	20	0.57	0.58	0.40-0.70	0.063
ECR	4	0.64	0.56	0.52-0.92	0.178	4	0.55	0.55	0.49-0.61	0.047
Other	7	0.53	0.56	0.24-0.77	0.176	7	0.63	0.61	0.43-0.93	0.123

Solution C (0.68 mg/l F, 200 mg/l SO_4, 2 mg/l Al, 2.5 mg/l $[NaPO_3]_6$).

Solution C contained 2.5 mg/l of hexametaphosphate in addition to the interferences added to Solution B. Phosphate is as likely to occur in domestic waters as is aluminum or sulfate because of widespread use in washing compounds; it may occur in raw surface water, on laboratory glassware used in fluoride analyses, in shallow wells located in urban areas or in wells near septic tanks. Due to ever increasing release of phosphates to the environment, no waters can be considered phosphate free until so determined.

No correction procedure other than distillation is offered for phosphate. The results obtained on the undistilled portion of Solution C emphasize the magnitude of the error introduced by this interference. The arithmetic mean of the SPADNS method is 0.82 mg/l; for the M & M it is 0.69; for S & S, 0.56 mg/l, for ECR, 0.90; and for the other methods 0.68 mg/l. The bar chart indicates that the SPADNS results are high, whereas the comparative procedures show a random distribution of high and low values. All procedures had a high standard deviation.

The same pattern persisted for Solution C distilled as for distilled portions of Solution A & B. The SPADNS and comparative procedures were brought into closer agreement and the means came within the acceptable $\pm$0.10 mg/l range. The standard deviation of the SPADNS results was similarly reduced.

From the data on Solution C, the following conclusions are drawn:

1. Hexametaphosphate produces a pronounced positive interference in the SPADNS and ECR procedures and a negative interference in the Scott-Sanchis method.

2. Interference from sulfate, aluminum, and hexametaphosphate can be effectively eliminated by distillation.

Statistical Summary, Solution C (0.68 mg/l)

Method	Undistilled					Distilled				
	No. of Analyses	Arith. Mean	Median	Range	Std. Dev.	No. of Analyses	Arith. Mean	Median	Range	Std. Dev.
SPADNS	53	0.82	0.81	0.56-1.66	0.153	53	0.72	0.73	0.24-1.22	0.092
M & M	17	0.69	0.70	0.28-1.06	0.166	16	0.68	0.67	0.31-0.97	0.068
S & S	20	0.56	0.55	0.43-0.67	0.142	20	0.67	0.68	0.55-0.80	0.071
ECR	4	0.90	0.80	0.79-1.21	0.283	4	0.76	0.76	0.71-0.81	0.092
Other	7	0.68	0.68	0.37-0.90	0.163	7	0.71	0.70	0.32-1.00	0.197

SUMMARY OF COMMENTS CONCERNING THE DISTILLATION PROCEDURE

The comments on the distillation procedure furnished by 46 participants are summarized as follows:

1. In general the method was found to be easy to use, requiring simple glassware and less attention than the standard Willard and Winter procedure.

2. Some of the laboratories reported carry-over of sulfate, although the sulfate values in the distillate were found to be approximately 30-50 mg/l.

3. A few of the laboratories felt that even the somewhat simple Bellack method was time-consuming and that distillation was not warranted for routine work.

4. The total elapsed time for the Bellack method is about the same as for the Willard and Winter, although operator attention is reduced in the newer procedure.

COMMENTS ON DISTILLATION PROCEDURES

LABORATORIES

No. 1

Bellack distillation: This method is much more simple than that for steam distillation.

No. 2

Bellack distillation: Method distills about 30 to 40 ppm of H_2SO_4. It is easy to control and requires little attention; however, it is slow. Comparative distillation - not used.

No. 3

Bellack distillation: 15 to 20 minutes are required to introduce the sample and raise temperature to start distillation. At maximum safe boiling activity, 30-35 minutes are required for 300 ml. 50 mg/l sulfates were consistently found in the distillate. Familiarity with the distillation was achieved before proceeding with samples. It is felt that any distillation requires too much apparatus, space, time, and dilligence to be used routinely in the public water-supply industry.

Comparative distillation: A modification of the Willard and Winter method, developed in this laboratory in 1955, using 100-ml sample in 40 ml H_2SO_4 and collecting 200 ml of distillate, operates on a 30-minute rerun cycle instead of a total of 50 minutes . . . plus 25 minutes to cool enough to introduce a new sample. Concentration of 200 ml of sample to about 100 ml, by boiling at $<$pH 8.0, and collecting 200 ml of distillate overcome the dilution factor of W & W method. Sample was insufficient to permit comparative distillation.

No. 4

Bellack distillation: No particular difficulty was encountered during this distillation. Most of the sulfates come over in the 175°C- to 180°C-temperature range. At no time did the sulfate content as (SO_4) of the distillate exceed 40 ppm. The use of two flasks should overcome the loss of time between distillation, when the temperature is allowed to drop to 120°C, before adding another sample.

Comparative distillation: All samples for fluoride analysis in this laboratory are distilled before making the fluoride determination. A 200-ml sample is used instead of 150

LABORATORIES

ml as directed in the Distillation Procedure of the Standard Methods, 10th Ed., pg. 99. Approximately 20 minutes are used for each distillation. Proper temperature control requires some attention.

No. 5 Bellack distillation: Sulfate carry-over in distillation.

A 56 ppm
B 45 ppm
C 58 ppm

No. 6 Bellack distillation: Although fairly slow this method requires relatively simple equipment and does not require constant attention.

No. 7 Bellack distillation: Distillation far too slow for routine procedure.

No. 8 Bellack distillation: This distillation was used for both procedures because it is our standard purification procedure.

No. 9 Bellack distillation: Minimum supervision required by this procedure has been found advantageous in our laboratory. Shielding and slower distillation do not eliminate sulfate carry-over, but our current fluoride method is not sensitive to small amounts in the distillate.

No. 10 Bellack distillation: Definite improvement over present standard method. Requires less attention and time and is less subject to sulfate carry-over.

No. 11 Bellack distillation: Solution B run as received.

No. 12 Bellack distillation: Very fine distillation procedure; we use it routinely. Sulfate in distillate runs about 25-30 mg per liter.

No. 13 Bellack distillation: This distillation is simpler than the Willard and Winter method for the determination of fluoride.

LABORATORIES

No. 14 Bellack distillation: This method provides greater freedom for the analyst and will afford considerable savings in reagents as compared with the Willard and Winter method. However, it appears to be more limited in application.

No. 15 Bellack distillation: We used a 750-watt heater and a standard 1000 ml phenol or water distillation unit. The time required for distillation was about 55 minutes. Operator time required was about 15 minutes. Sulfate carry-over was 38, 39 and 32 mg/l in three trials. This distillation, if done routinely, could be automatically stopped by a temperature-control unit, which would reduce operator time. Our own system distills a sample in about 25 minutes and requires 3 to 5 minutes of operator time. It produces a distillate with less than 10 mg/l of sulfate.

Comparative distillation: We use the method of Frazier and Oldfield, Public Health Reports, July, 1953, modified so that the rate of flow, the distillation temperature, separation of the wasted fraction of distillate, and termination of the distillation are all automatically controlled.

No. 16 Bellack distillation: This technique is superior to the steam distillation method. Each of the distilled samples showed a negative test for sulfates. When adding second aliquot to warm flask, some steaming was noted at 105°C, but there was no apparent loss of fluoride as evidenced from results on Sample A.

Comparative distillation: Bellack method was used for all distillations.

No. 17 Bellack distillation: This appears to be a good procedure for distilling fluorides. It requires very little attention during the distillation and the distillate was found to contain very little sulfate carry-over.

Comparative distillation: The distillation procedure as indicated in the 10th Edition of Standard Methods is used by this laboratory on samples requiring distillation. It

LABORATORIES

has been found that the method requires constant attention to prevent carry-over of sulfates into the distillate.

No. 18 Bellack distillation: We have been using this distillation procedure for the past 8 months and find it much less trouble for routine work than the steam distillation.

Comparative distillation: As noted above we have been using the Bellack distillation procedure.

No. 19 Bellack distillation: This procedure has the advantages of simplicity of equipment and does not require constant attention. It is an ideal method for infrequent fluoride determinations. However, there is no improvement in the total time required for distillation over that of the Willard and Winter method. There is also the possibility of some sulfate contamination.

Comparative distillation: The Willard and Winter steam distillation method at 135°C is used in our laboratory. For water samples, a 100-ml to 500-ml sample is made slightly alkaline with sodium hydroxide and concentrated to approximately 25 ml. Then a few drops of silver perchlorate solution are added to precipitate the chlorides and 25ml of 70% perchloric acid. The sample is steam distilled at 135°C until 250 ml of distillate has been collected.

No. 20 Bellack distillation: On all distillations the distillate totaled 300 ml when the sulfuric mixture reached 180°C.

Comparative distillation: No comparative distillation method was used.

No. 21 Bellack distillation: This method is more convenient than the Willard and Winter distillation primarily because less time and attention are required. Quantitative recovery of fluoride from known solutions and from water samples was excellent.

LABORATORIES

Comparative distillation: This laboratory uses the Willard and Winter steam distillation from a perchloric acid solution at 135°C. Using the SPADNS method, slightly low results were obtained. However, using the Scott-Sanchis method or the thorium nitrate titration, results more comparable to those using the Bellack distillation were obtained.

No. 22 Bellack distillation: This method is much easier to use than the distillation procedure we use. Should be safer to use also. I don't believe there is much danger of the perchloric acid exploding when used with steam but one is always apprehensive.

No. 23 Bellack distillation: The results obtained for Solution A indicate an approximate 12% loss of fluoride in the Bellack distillation procedure when the SPADNS method is used. That the same loss is not apparent when the Scott-Sanchis method is employed cannot be taken too seriously since reading against wet standards, personal judgment and reporting only to the first decimal place are involved.

In view of this apparent loss due to distillation, the greater decreases in fluoride findings for Solution B and C must be interpreted as due to a combination of distillation losses plus ridding the solutions of interfering materials.

This distillation procedure does have distinct advantages over the Willard and Winter method, including the use of simpler apparatus and less attention required of the analyst.

Comparative distillation: Shortages of personnel and time did not permit comparative distillations. We intend to compare the Bellack and Willard and Winter distillations as soon as time permits, especially in view of our apparent losses on Sample A.

No. 24 Bellack distillation: The procedure was a long and tedious method requiring constant attention. The elaborate distilling apparatus required much space.

LABORATORIES

Careful technique is a must in the initial preparation of the Bellack boiling mixture. Constant attention was required when the cut-off point of 180°C and 300 ml of distillate was reached. The time involved in waiting for the acid mixture to cool down to 120°C was long. We added slowly small portions of sample with constant swirling to keep the contents from over heating exothermocally. To keep the mixture cool and minimize loss of fluoride during addition of sample, a water bath was used. Prolonged use of the acid mixture resulted in the darkening of the boiling mixture due to deterioration of the rubber stopper holding the thermometer.

Results analyzed indicated that the values obtained from distilled samples are closer to the actual fluoride content than undistilled samples.

Comparative distillation: The distillation method is not used in this laboratory for fluoride determination.

No. 25 Bellack distillation: We find that approximately 80 mg/l of sulfate is carried over using the procedure and equipment as specified. Supplementary tests have indicated that erratically as much as 0.1 mg/l of fluoride is lost in this distillation. The technique is quite convenient.

No. 26 Bellack distillation: Very simple method.

Comparative distillation: Temperature very hard to maintain.

No. 27 Bellack distillation: Acid boiling solution has a dirty look after all distillations were made. Could be from boiling chips.

Comparative distillation: Not used.

No. 28 Bellack distillation: No comment.

No. 29 Bellack distillation: This distillation technique was tested and found satisfactory if proper precautions for sulfate carry-over are followed.

Comparative distillation: Not used.

LABORATORIES

No. 30

Bellack distillation: No comments.

Comparative distillation: None used.

No. 31

Bellack distillation: This method seems quite simple and satisfactory; however, due to the importance of stopping distillation at the right temperature, this distillation method will be prohibitive in terms of laboratory time except for referee samples.

Comparative distillation: Not used.

No. 32

Bellack distillation: Method is simple and reproducible. Results did not vary from one distillation to another. No difficulty with sulfate carry-over if distillation is stopped when it reaches exactly 180°. We hope this method proves reliable since it is certainly a great improvement over the Standard Methods (10th Edition) distillation.

Comparative distillation: Routine distillation (Standard Methods, 10th Ed.). Although we did not do comparative distillations, we routinely use this method when interference warrants. We find it very time consuming as it requires constant attention for temperature control; also presents a hazard from sulfate carry-over. This distillation procedure constitutes a source of error, which in some cases is greater than the interfering ions.

No. 33

Bellack distillation: Temperature control must be closely regulated to obtain fairly comparable results. Distillation does not appear necessary for the removal of some interfering ions. In spite of rigid temperature controls, results had a wide variance on triplicate analysis. No explanation for the consistently low third run on the distilled sample.

Comparative distillation: In routine analysis from finished waters, the pretreatment by distillation is omitted. When samples are suspected of containing interfering ions, the sulfuric acid distillation procedure described in the 10th Edition of Standard Methods is followed.

LABORATORIES

No. 34

Bellack distillation: We have been using this method, slightly modified, for two years. Our apparatus has all-glass joints. The distilling flask has a thermometer well and the distillate does not come in contact with any rubber stoppers. We modify further by using half quantities for distilling, i. e., 100 ml H_2SO_4 to 200 ml water boiled, etc., to 180°C, and 150 ml sample and distill over 150 ml.

Comparative distillation: Our modified Bellack method, by using half quantities as mentioned above, permits only 30 to 35 ppm of sulfates to be distilled over into the distillate. This, of course, has no effect upon Scott-Sanchis reagent.

No. 35

Bellack distillation: Temperature control requires constant attention of the analyst. If the SPADNS method is considered for use on distilled samples, the possibility of sulfate carry-over during distillation below 180°C is not to be overlooked.

Comparative distillation: Our standard perchloric acid-steam method is much less time consuming per sample, and, with the use of Fisher-Serfass Electronic Relays, temperature control is no concern.

No. 36

Bellack distillation: Recovery good over 95%. Temperature control not required thereby relieving operator for other duties. Distillation time less than current method. Amount of distillate sufficient to run several methods and duplicate analyses on one sample.

Comparative distillation: Steam distillation - recovery is not consistent, varies from over 95% to under 95%. More time consuming, 35-40 minutes. Distillate sufficient for only one test.

No. 37

Bellack distillation: This procedure is relatively easy to perform but requires a large volume of water sample (300 cc) and is somewhat slow when running a number of samples. In our hands the results obtained with Solution A and B using this method were not entirely consistent.

LABORATORIES

Comparative distillation: The apparatus used was distillation apparatus A with revisions, found on page 100 of Standard Methods for the Examination of Water, Sewage, and Industrial Wastes, 10th Edition, 1955. This method requires less water sample, 50 cc, and allows the continuous addition of samples when running a large number.

No. 38B — Bellack distillation: Fits in very nicely for control work.

No. 39 — Bellack distillation: Easy but time-consuming.

No. 40 — Bellack distillation: In paragraph 2 of the distillation procedure, it should be emphasized that careful, thorough mixing after addition of 300 ml of sample to the distillation flask is essential to prevent a possible explosion as heat is applied.

No. 41 — Bellack distillation: Commendable method; no difficulties were encountered.

No. 42A — No comment.

No. 42B — Bellack distillation: Distilled according to Bellack distillation procedure. Read 1 cm cell - Beckman Model B.

Comparative distillation: Steam distillation 135°C to 140°C, starting with 100 ml and distilled 200 ml. Read 23 mm Round Cuvette - Beckman Model B.

No. 42C — No comment.

No. 42D — No comment.

No. 43 — Bellack distillation: The Bellack distillation is much simpler than the Standard Methods procedure, but considerable bumping action was encountered during the distillation, with each distillation requiring an overall time of approximately 1 1/2 hours.

Comparative distillation: Since no method was currently in use for the determination of fluoride, no comparative methods were used.

LABORATORIES

No. 44 — No comment.

No. 45 — Bellack distillation: The Bellack distillation is a very simplified operation which allows the technician to be free for other work while the distillation is in progress.

Comparative distillation: None used.

No. 46A — Bellack distillation: Slower than Standard Methods.

No. 47 — No comment.

No. 48 — Bellack distillation: Difficulty was experienced with the amount of sulfate carry-over in the distillation of these samples. The procedural outline was followed exactly but, nonetheless, the amount of sulfate distilled over exceeded the 30-40 mg found by the author to be most representative. The method is simple and rapid otherwise.

No. 49 — Bellack distillation: Much more simplified than past published distillation procedures, and a great deal easier than our present one. Seems to give results closer to the grand average than our present one.

Comparative distillation: Distilled from sulfuric acid in all-glass apparatus. Similar to Standard Methods procedure except that distilled water is added slowly to control the temperature instead of steam. Specially designed glassware, purchased from Martin & Company in Evanston.

No. 50 — Bellack distillation: A boon to the monthly fluoride routine. Much less thermometer watching - much more other work can be done while samples are distilling. More distillations can easily be run at once, with proper glassware available.

Comparative distillation: Tedious distillation to do on monthly sample group. Must check on temperature every few minutes, that it has not dropped or raised out of set limits. Time consuming and hard on the feet. Lengthier, in that our results have shown greater final accuracy when samples are concentrated to begin with, and so have this additional step.

SUMMARY OF COMMENTS ON SPADNS METHOD

Comments concerning the SPADNS method are summarized as follows:

1. Many laboratories concluded that the SPADNS method was superior to comparative methods in elapsed time and ease of manipulation.

2. The color-development time factor for the elimination of aluminum interference created some difficulty.

3. In some cases comparative methods were preferred because of experience and/or special modifications to eliminate interferences.

4. A few laboratories found that the SPADNS dye was disagreeable to use because of adsorption on glassware and hands.

COMMENTS ON SPADNS PROCEDURE

LABORATORIES

No. 1

SPADNS Method: Less time consuming, apparently less sensitive to interferences.

Comparative Analytical Method: Have been using it for about 3 years in this lab.

No. 2

SPADNS Method: Method has high sensitivity. Interferences for direct use are unknown because of unknowns in samples.

Comparative Analytical Method: Scott-Sanchis with Beckman Model B.

No. 3

SPADNS Method: The color intensifies in first 20 minutes, which upsets the possibility of evaluating Al interference as prescribed in the literature. A minimum of 10 minutes for color development is necessary. Insufficient dye precluded a study of the time factor. We boughta supply of the dye but it did not arrive in time to use in the present evaluation; however, it seems to have some potentialities which we plan to investigate.

Comparative Analytical Method: Scott-Sanchis. The aluminum in B hydrolyzed and flocculated to a degree that uniform aliquots were probably not obtained, accounting for the fluctuation in the undistilled results on the comparative procedure. Routine analyses are run on filtered samples, so this variation would not ordinarily appear. The proportions of the interfering substances on the SPADNS dye in both B and C solutions, but especially B, seem to be in the range that nearly cancel each other. It is felt that better evaluation would be attained if one sample had a considerably decreasing effect, and the other had a significantly increasing effect.

No. 4

SPADNS Method: No comments.

Comparative Analytical Method: No difficulty in using the Megregian-Maier Method, Standard Methods, 10th Ed., pp. 101, provided the sample is distilled before the color is developed.

LABORATORIES

No. 5

SPADNS Method: No comments.

Comparative Analytical Method: No comments.

No. 6

SPADNS Method: This appears to be an easy method to use and gives good checks, but requires fairly large amounts of reagent. It would be necessary to find the effect of aging of the reagent, as a standard curve is used. Of course, the effects of this or other variables could be eliminated by running a new curve each time. However this procedure would also increase the time necessary for the analysis.

Comparative Analytical Method: The Scott-Sanchis method for routine control on finished waters is simple, rapid, and appears to give adequate results. Using visual comparison, the effect of variations in the reagent is eliminated.

No. 7

SPADNS Method: No comments.

Comparative Analytical Method: Fast, simple dilution of prepared reagents. Sulfates could interfere in some waters.

No. 8

SPADNS Method: This method has the potential of saving time in the laboratory both from the reagent addition and the color development time. Based on these results the SPADNS method may be more precise than the comparative method.

Comparative Analytical Method: No comments.

No. 9

SPADNS Method: Until a 15- to 30- minute reaction time was used, difficulty in establishing a reproducible calibration curve was encountered. A similar amount of time was used for color development in the unknowns. Some gain in time over present method, but if unexpected high fluorides are encountered, gain becomes minimal. Permanence of color on equipment, fingers, and table tops somewhat objectionable.

LABORATORIES

Comparative Analytical Method: Sulfates present in natural samples or distillates do not seem to interfere. Reagents are stable, and for a large number of samples the minimum amount of manipulations required are ideal. Easier to anticipate high fluorides within moments of sample preparation.

No. 10

SPADNS Method: Requires more time for large number of samples than Scott-Sanchis method with visual comparison. This laboratory cannot use a 1-cm light path on photometer (spectronic 90, Bausch & Lomb), where shortest light path is 1/2 inch. Color intensity of dye too great. Method does not appear to be reproducible.

Comparative Analytical Method: No comments.

No. 11

SPADNS Method: Solution B filtered before running test. Results given are after a 4-hour wait (Solution A & C). The results of A were 0.07 higher at 5 minutes and C was 0.06 lower at 5 minutes.

Comparative Analytical Method: Solution B filtered before running test.

No. 12

SPADNS Method: Rapidity and simplicity of this procedure and stability and reproducibility of standard curve make the method attractive. Only serious fault is its sensitivity to sulfation-ion concentration. For routine use on waters containing sulfate concentrations below interference level this method could be used to advantage.

Comparative Analytical Method: Scott-Sanchis method somewhat time-consuming although not necessarily in terms of man hours. Its relative freedom from interference makes it useful for general routine use.

No. 13

SPADNS Method: It seems that this method would have a greater sensitivity than that of the Scott-Sanchis and the time consumed would be less.

LABORATORIES

Comparative Analytical Method: The Scott-Sanchis method is fairly rapid but perhaps not as accurate as a distillation procedure. In comparing the SPADNS and Scott-Sanchis method I believe that the former is a better method for fluoride determinations.

No. 14

SPADNS Method: We found little to recommend this method over the Scott-Sanchis currently employed in our laboratory.

Comparative Analytical Method: No comments.

No. 15

SPADNS Method: This method is quite easy to handle, but appears to have less tolerance for interfering substances than the technique we use routinely. The SPADNS has about the same range as the one we use, but, as described, considerably less sensitivity.

Comparative Analytical Method: We use the Megregian Eriochrome Cyanine R method as modified by Thatcher. The addition of Barium to the reagent makes it almost completely free from influence by sulfates. We routinely set samples up on one day and read them on the next day. Centrifuging would make results available in a shorter time, if this became important.

No. 16

SPADNS Method: Due to high absorbance of samples and reference solution at a wavelength of 570 mμ, we find that it requires a completely charged battery to obtain good, steady transmittance readings with our Coleman Spectrophotometer.

Comparative Analytical Method: We use the Scott-Sanchis method regularly in our laboratory. It is simple, convenient, and accurate when interfering ions are absent.

No. 17

SPADNS Method: This seems to be a simple, rapid, and satisfactory method for determining fluorides if interferences are not present.

Comparative Analytical Method: A good procedure but somewhat time-consuming. On samples containing high

LABORATORIES

sulfates and chlorides, equivalent amounts of these ions are added to each of the standards. Alkalinity is neutralized with nitric acid. Color is removed with activated carbon and turbidity by filtering. Chlorine is removed by sodium arsenite. Phosphates and aluminum interfere seriously. The method is satisfactory as a routine procedure for untreated water when sulfate and chloride contents are known.

No. 18

SPADNS Method: Much neater procedure than the Megregian-Maier procedure. Excellent for routine work. The reference solution has been stable for one week with no indication of fading.

Comparative Analytical Method: We are currently using the Megregian-Maier Method. This method is lacking in that the color changes with time. SPADNS method appears to be superior.

No. 19

SPADNS Method: This method has the advantage of a single stable reagent.

Comparative Analytical Method: The Eriochrome Cyanine R spectrophotometer method was used. Reference: H. M. Nielsen, Analytical Chemistry, 30, 1009, 1958.

No. 20

SPADNS Method: These results were from the second set of solutions we received.

Comparative Analytical Method: These results were obtained from the first set of solutions we received. As indicated in the statistics, B and C solutions were also run after filtration through a millipore filter, before distillation.

No. 21

SPADNS Method: The time needed per sample is less than either the Scott-Sanchis method or the thorium nitrate titration. A big advantage appears to be that fewer samples would need distillation in order to determine the true fluoride content. We are impressed with the simplicity and rapidity of this method. Aluminum

LABORATORIES

still presents some difficulty, as demonstrated by Solution B. The initial readings would indicate 0.51, 0.54, and 0.47 mg F/l. The waiting period overcomes this interference, or better still, the Bellack distillation can be used.

Comparative Analytical Method: The Scott-Sanchis method has always given good results on the water samples which we have analyzed. The chief disadvantages to us are the time required for analysis and the interference of phosphate.

No. 22 SPADNS Method: No comments.

Comparative Analytical Method: For our color evaluation we use Nessler tubes (.01 mg F) between each color standard. Should be fairly accurate but probably not as accurate as the spectrophotometer.

No. 23 SPADNS Method: This method offers greater accuracy than the Scott-Sanchis and avoids the personal judgment element inherent in any procedure dependent on wet color standards. This method has a decided advantage over previously introduced photometric fluoride procedures in that no corrections for sulfate or aluminum are required. The saving of time is another positive factor.

Comparative Analytical Method: Scott-Sanchis fluoride results are read and reported to a single decimal place; possible human variations of judgment and the difficulty of differentiating to the hundredth of a part per million do not seem to justify otherwise. The time factor, the need for preparing fresh wet standards, and the inevitable introduction of human errors in reading the color systems favor adoption of the SPADNS method.

No. 24 SPADNS Method: The method was good and reliable when distilled water samples were used. On the other hand, the undistilled samples required a 2-hour bleaching period to eliminate the interferences. The result values on

LABORATORIES

Solution A without interferences were quite realistic between the SPADNS method and our present method. Appreciable differences were noted in the results of Solutions B and C in both methods. Comparison of results obtained showed that the SPADNS method, without distillation and with interfering ions, showed an increase in fluoride. Solution B, without distillation, averaged 0.78 mg/l fluoride and, distilled, averaged 0.43 mg/l fluoride. Solution C, without distillation, averaged 0.87 mg/l fluoride and, distilled, averaged 0.60 mg/l fluoride in comparison to our present method. Our present comparative method showed in Solution B, without distillation, averaged 0.2 mg/l fluoride and, distilled, averaged 0.5 mg/l fluoride. Solution C, without distillation, averaged 0.5 mg/l fluoride and, distilled, averaged 0.7 mg/l fluoride which contradicts the results obtained in the SPADNS method. The results cannot be compared objectively due to the unknown amount of fluoride in the samples.

Comparative Analytical Method: The zirconium-alizarin method used at this laboratory uses the same theory as SPADNS method - bleaching out the red dye. Distillation is not required to eliminate the interferences. Interferences are eliminated as follows: Bicarbonates are neutralized with nitric acid in excess of 12 mg. When chlorides are in excess of 1,000 ppm and sulfates are in excess of 500 ppm a given amount of chloride and sulfate are added to eliminate these interferences. Activated charcoal is used to eliminate colored matters in the samples. After adding the zirconium-alizarin indicator solution to the samples, they are left standing overnight for complete bleaching action, and in the morning they are read with visual comparison to the standards. The fluorides are measured to tenths instead of to hundredths as in SPADNS method.

No. 25

SPADNS Method: We attempted to use this method on a Klett colorimeter (industrial model) but were unable to adjust the reference solution to zero using a light path greater than 2 mm because of the high intensity of the color of the reference solution. Results reported were obtained on a Beckman Model B spectrophotometer using a sensitivity of 3 and a slit width of 0.2 mm.

LABORATORIES

Comparative Analytical Method: Modified Thatcher procedure enclosed. Enclosed summary of the results of fluoride tests on a fluoridated water show that using this procedure the results check extremely well with the amount of fluoride added. We find this method to be more convenient than any other we have tried. Its only disadvantage is that one must wait overnight before making readings.

No. 26

SPADNS Method: The fact that there is no waiting period saves considerable time.

Comparative Analytical Method: No comment.

No. 27

SPADNS Method: B sample had Al $(OH)_3$ precipitate in bottle. Took 3 readings on spectrophotometer. Final reading 1 1/2 hours after mixing. (Comp. Method filtered).

C sample took 3 readings; final reading 1 hour after mixing.

Comparative Analytical Method: B sample was filtered due to floc suspension. Standards were set up in 1/2 ppm increments.

No. 28

SPADNS Method: No comment.

Comparative Analytical Method: No comment.

No. 29

SPADNS Method: Method holds advantages of immediate reading and straight line curve.

Comparative Analytical Method: The Scott-Sanchis colorimetric method shows early dip in the otherwise straight line curve.

No. 30

SPADNS Method: We were short somewhat on the supply of the SPADNS reagent because some had spilled in transit. However, we maintained the concentration called for in the procedure.

LABORATORIES

Comparative Analytical Method: We used the Megregian-Maier method, page 101, 10th Edition, Standard Methods, without distillation. Not knowing the possible interferences in Samples A, B, and C, we were in doubt as to the direct application of this procedure without distillation. We did not add the arsenite solution in this analysis.

No. 31

SPADNS Method: We much prefer this method to the visual methods. We think, perhaps, our results with this method would have shown a smaller range of values if we had had enough SPADNS reagent to make a trial run. We did not have enough reagent to complete the last run.

Comparative Analytical Method: We have found considerable disagreement as to color among operators using this method.

No. 32

SPADNS Method: Method is both simple and rapid. Results on individual samples of the same dilution did not vary. Results reproducible. Method a great time-saver due to stability of mixed reagents and immediate color development. Time element not critical. Possibility of using one water sample for quantitative fluoride and qualitative aluminum. Limited time prevented further experimentation at this time. At a later date we plan to experiment with this method using various quantities of known interfering substances found in the potable water of this state. We have many sources with sulfate exceeding 200 mg/l.

Comparative Analytical Method: Megregian-Maier method, 10th Ed., Standard Methods. We found this method to be the best available up to this time. Very satisfactory for our routine analyses. One-hour waiting period a constant source of annoyance. Due to progressive color development, the time element is critical, consequently only a few tests can be carried out at one time without careful time control between addition of reagents and reading of samples. Our standard curve is set up using 50 mm cylindrical cells.

LABORATORIES

No. 33

SPADNS Method: Procedure seemed to give higher results when using the Scott-Sanchis method, a possible indication of interfering ions which would be separated by a preliminary distillation step.

Comparative Analytical Method: The Scott-Sanchis method requires a one-hour waiting period, but the results reported to the nearest 0.05 ppm are generally reproducible. In Solutions B and C, interfering ions (probably aluminum) were found to be present and gave lower, less comparable values in the undistilled sample. On pretreatment by distillation, higher, more comparable results were obtained.

No. 34

SPADNS Method: The SPADNS method does overcome many of the difficulties or faults of the other spectrophotometric methods. However, the extinction-coefficient is too low, and the reverse slope of the curve makes this method almost impossible for a routine laboratory operation. A new approach to the fluoride method that would give a positive curve would be welcomed. We find that good results are obtained by arbitrarily setting the zero fluoride standard at a desirable optical density such as 0.500.

Comparative Analytical Method: Our comparative analytical method, without distillation, is one of removing any aluminum in the sample by adjusting the pH of the sample to 6.6 which is in the isoelectric zone for the insolubility of aluminum hydroxide and filtering. Very good results are obtained compared with those on the distilled portion.

No. 35

SPADNS Method: The procedure is easy to perform. However, the color developed by undistilled samples of B & C and read immediately, 2 and 4 hours later, reflected steadily decreasing optical densities as measured by a Beckman Model B Spectrophotometer. Optical density readings of distilled samples made initially agreed with those made 2 hours later. Variable results were obtained when variable sized aliquots of the distilled and undistilled solutions were employed.

Comparative Analytical Method: No comment.

LABORATORIES

No. 36

SPADNS Method: Much less time-consuming than current method. Reagents for test can be made in less time than the reagent for current method. Waiting period eliminates aluminum interference. Increase in results due to phosphate interference is less than the decrease shown by our current method.

Comparative Analytical Method: Lamar Method Time-consuming, requires 1-hour waiting period. Readings are visual and estimated within a range of . 2 mg. Preparation of reagent is time-consuming due to standardization of acid and mixing of solutions. Aluminum and phosphate interferences result in considerable depression of results.

No. 37

SPADNS Method: Due to the relationship of the O. D. to mg/l of F., the standard curve is quite steep and requires a close adherence to proportions in order to prevent errors. Solution B was found to contain aluminum. As was indicated in the procedures, the samples were allowed to stand for 1 hour. During this period, the interference was eliminated and readings were found to correspond closely to the samples of B which were distilled.

Comparative Analytical Method: A modified SPADNS method was used. In this procedure, a reference solution is not used. Using cells of 25-mm diameter and 95-mm length, we have determined that a solution of 1 ppm F with SPADNS (5-cc/25-ml sample) reads 0. 54 in the Beckman Model B. This standard solution is then used to "zero" the spectrophotometer when running samples. On the basis of 1 ppm, we have plotted a reference table. This method is faster than using 10-mm cells when a large number of samples are to be run. Also, we have had good comparison with water plants using both the Scott-Sanchis and Megregian-Maier methods.

No. 38B

SPADNS Method: Good.

Comparative Analytical Method: Scott-Sanchis. Extremely sensitive.

LABORATORIES

No. 39

SPADNS Method: Easy and Quick.

Comparative Analytical Method: This method is based upon the reaction of the red zirconium-alizarin color with the fluoride ion to form a colorless ion of zirconium and fluoride. The reaction forms free alizarin sulfonic acid which is yellow in solutions. The photometric measurement is taken at 530 mμ on a suitably calibrated photometer. The most serious interference in this method is due to the presence of any aluminum which produces too low results. As a general rule, each 0. 2 ppm of aluminum depresses the result of fluoride by 0. 1 ppm.

No. 40

SPADNS Method: Accurate measurement of the 10 ml of mixed reagent which is added in step 3 of the analysis procedure is very critical. Even very slight differences in volume apparently affect the transmittance of the final solution materially. It is also essential that the temperature of the final solutions be the same (within $\pm$ 2°C) before transmittance is measured. When these two precautions were observed, identical transmittance readings were obtained for triplicates. A Beckman Model B spectrophotometer was used to measure transmittance.

Comparative Analytical Method: Although this method involves visual comparison of the sample colors with those of standards containing increments of 0. 1 ppm of fluoride, identical values accurate to 2 decimals were obtained for each set of triplicates as follows: It was observed that it was impossible to distinguish any difference in color among the three samples in each set of triplicates. The color of one sample from each set was then compared to that of the standard with the next lower and next higher color concentration, and a ppm value assigned to the set by interpolation.

No. 41

SPADNS Method: A good method with results that are reproducible. SPADNS reagent powder (Eastman #7309) is difficult to obtain. 4-5 months elapsed before our first order of SPADNS was filled. Undesirable red stain is produced on articles such as towels, hands.

LABORATORIES

Comparative Analytical Method: Color-comparator wheel in visual comparator is faded; a method of more precision is welcome and is in order.

No. 42A — No comment.

No. 42B — SPADNS Method: 1-cm cell, Beckman Model B

Comparative Analytical Method: We use SPADNS method except we use a 23-mm round cuvette. Beckman Model B.

No. 42C — No comment.

No. 42D — No comment.

No. 43 — SPADNS Method: Each new volume of working reagent gave differing standard curves, even though each was prepared from the same stock solutions. In view of this, a standard curve was made for each set of samples being analyzed.

Comparative Analytical Method: No comment.

No. 44 — No comment.

No. 45 — SPADNS Method: The SPADNS method for fluorides is a quick and efficient method with a minimum of interference to be compensated. It gives results which are readily reproducible.

Comparative Analytical Method: The Megregian-Maier method for fluorides is very time-consuming and entails much work in testing for the many interferences which must be compensated to obtain accurate results.

No. 46A — SPADNS Method: Tremendous advantage over current method using 11 Nessler tubes just for standards.

Comparative Analytical Method: No comment.

No. 47 — SPADNS Method: This method was not performed until the date indicated on the tabulation sheet, and there was

LABORATORIES

a considerable amount of a grayish white flocculation and turbidity which was removed by filtration before testing with the SPADNS working reagent. It was thought that the time elapsed might have caused an effect on the fluoride readings of the SPADNS results on the samples containing interferences.

Comparative Analytical Method: The SPADNS procedure does not state any effect that time might have between the addition of the SPADNS working reagent and the reading of the sample. In the Megregian-Maier procedure, the factor is very critical. Solution B, without distillation by the SPADNS method, was read again after all the other determinations had been made, which was about twenty minutes, and the effect on the reading was negligible.

No. 48

SPADNS Method: Our findings in this study indicate that the sulphate ion interferes with the determination of fluoride by this method. A graph illustrating this fact has been enclosed. Two sets of results, therefore, are submitted - one showing results without this sulphate correction and the other giving the results with the sulphate correction applied.

Comparative Analytical Method: The method used is a modification of the Megregian Eriochrome Cyanine R method. Again, the sulphate ion interferes with the determination of fluoride. The effect of this interference is additive. An equivalent amount of the sulphate ion concentration found in the sample in which the fluoride is to be determined is added to the blank and to the standard (or standards). The net result is a cancellation of the sulphate ion.

No. 49

SPADNS Method: This method gives the most reproducible curve we have found. However, a longer light path might make it more readable.

LABORATORIES

Comparative Analytical Method: This is essentially the Megregian-Maier method described in the 10th Edition of Standard Methods with the modifications that the sample size is reduced to 50 ml and the zirconium and alizarin reagents mixed an hour prior to use. Then 5.0 ml of the mixed reagent is added to each tube. The samples are read on a Klett-Summerson colorimeter with a 520 mμ filter.

No. 50

SPADNS Method: More potent acid fumes from solution make one swear off pipetting by mouth. Gradual change in readings occurred, perhaps due to time. Run at 25-minute intervals for several hours, slid up the scale, not always in direct relationship to time before; therefore, not all curve points landed where they should have each time. Finally settled on a timed relationship so that each sample stood the same length of time before reading, which helped the situation immensely. Keeps one busy making new curves! Had no great temperature changes to deal with - only 0.5°C to 1°C difference at the most.

Comparative Analytical Method: Not greatly different in effort and lab working time. Perhaps more familiarity with this method tends to make us think that a good straight-line curve is more easily arrived at than with the SPADNS, as possible variations are already known and guarded against.

SUMMARY OF REPORT

The data reported by the 53 participating agencies of the study, Sample Type III-B (Water, Fluoride) permit the following conclusions:

1. In the absence of interfering substances, the average laboratory can routinely produce results within the $\pm$ 0.10 mg/l limit at the 1.0 mg/l level, employing the SPADNS method.

2. On Solution B containing sulfate and aluminum interferences, the SPADNS method gave the best results on the undistilled samples as compared to all other methods employed.

3. Hexametaphosphate produced a pronounced positive interference in the SPADNS method, but this interference was effectively eliminated by the Bellack distillation. Data indicate that distillation is particularly essential when phosphate is present in a sample.

4. The Bellack distillation was effective in removing interfering substances incorporated in the sample.

5. The SPADNS method was superior to some of the comparative methods and equivalent to all other methods used.

COMPARISON OF REPLICATE VALUES

Solution A (0.83 mg/l Fluoride), Undistilled

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
SEC	0.87 0.88 0.89	0.88	---- ---- ----	----	None
1	0.75 0.85 0.80	0.80	0.80 0.86 0.80	0.82	Megregian-Maier
2	0.87 0.85 0.85	0.86	0.75 0.80 0.70	0.75	Scott-Sanchis
3	0.81 0.86 0.82	0.83	0.78 0.78 0.80	0.79	Scott-Sanchis
4	0.80 0.82 0.83	0.82	0.86 0.86 0.89	0.87	Megregian-Maier
5	0.88 0.85 0.80	0.84	0.83 0.85 0.85	0.84	Megregian-Maier
6	0.83 0.83 0.82	0.83	0.76 0.76 0.76	0.76	Scott-Sanchis
7	1.35 1.32 1.35	1.34	1.00 1.00 1.00	1.00	Hellige
8	0.75 0.75 0.75	0.75	0.80 0.80 0.80	0.80	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
9	0.70 0.70 0.88	0.69	0.84 0.86 0.84	0.85	Megregian-Maier
10	0.85 0.96 0.96	0.92	0.80 0.85 0.85	0.83	Scott-Sanchis
11	0.79 0.78 0.79	0.79	0.81 0.81 0.81	0.81	Megregian-Maier
12	0.82 0.80 0.84	0.82	0.80 0.80 0.80	0.80	Scott-Sanchis
13	0.90 0.90 0.90	0.90	0.80 0.80 0.80	0.80	Scott-Sanchis
14	0.80 0.80 0.80	0.80	0.85 0.80 0.80	0.82	Scott-Sanchis
15	0.98 0.96 0.92	0.95	0.82 0.81 0.85	0.83	ECR
16	0.78 0.80 0.80	0.79	0.80 0.80 0.80	0.80	Scott-Sanchis
17	0.84 0.86 0.82	0.84	0.82 0.81 0.82	0.82	Scott-Sanchis

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
18	0.84 0.81 0.80	0.82	0.79 0.79 0.80	0.79	Megregian-Maier
19	0.76 0.76 0.76	0.76	0.92 0.92 0.92	0.92	ECR
20	0.90 0.90 0.90	0.90	1.00 1.00 1.00	1.00	Hellige
21	0.81 0.82 0.82	0.82	0.85 0.85 0.85	0.85	Scott-Sanchis
22	0.82 0.82 0.82	0.82	0.80 0.80 0.80	0.80	Scott-Sanchis
23	0.81 0.81 0.81	0.81	0.80 0.80 0.80	0.80	Scott-Sanchis
24	0.76 0.73 0.73	0.74	0.90 0.90 0.90	0.90	Megregian-Maier
25	0.80 0.82 0.83	0.82	0.80 0.80 0.79	0.80	ECR
26	0.92 0.92 0.92	0.92	0.86 0.86 0.86	0.86	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
27	0.65 0.66 0.66	0.66	0.63 0.63 0.63	0.63	Scott-Sanchis
28	0.93 0.90 0.90	0.91	---- ---- ----	----	None
29	0.84 0.89 0.86	0.86	0.88 0.88 0.88	0.88	Scott-Sanchis
30	1.17 1.25 1.27	1.23	0.68 0.45 0.82	0.65	Megregian-Maier
31	0.80 0.80 0.90	0.83	1.00 0.70 0.70	0.80	Scott-Sanchis
32	0.85 0.85 0.87	0.86	0.80 0.80 0.85	0.82	Megregian-Maier
33	0.82 0.82 0.85	0.83	0.78 0.82 0.84	0.81	Scott-Sanchis
34	0.80 0.82 0.78	0.80	0.80 0.80 0.80	0.80	Scott-Sanchis
35	0.85 0.73 0.85	0.81	0.82 0.79 0.78	0.80	Thorium Nitrate

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
36	0.91 0.89 0.87	0.89	0.78 0.82 0.80	0.80	Lamar
37	0.81 0.78 0.76	0.78	0.84 0.84 0.86	0.85	Modified SPADNS
38B	0.84 0.84 0.86	0.85	0.78 0.77 0.78	0.78	Scott-Sanchis
39	0.84 0.84 0.84	0.84	0.83 0.80 0.80	0.81	Megregian-Maier
40	0.77 0.77 0.77	0.77	0.76 0.76 0.76	0.76	Thrun
41	0.80 0.80 0.80	0.80	0.80 0.80 0.80	0.80	Scott-Sanchis
42A	0.82 0.84 0.83	0.83	---- ---- ----	----	None
42B	0.80 0.82 0.82	0.81	0.82 0.82 0.78	0.81	SPADNS with steam distillation
42C	0.88 0.88 0.89	0.88	0.79 0.79 0.80	0.79	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
43	0.85 0.85 0.84	0.85	---- ---- ----	----	None
44	1.08 1.05 0.95	1.03	0.82 0.75 0.84	0.80	Not Identified
45	0.82 0.83 0.83	0.83	1.30 0.68 1.00	0.99	Megregian-Maier
46A	0.80 0.80 0.80	0.80	0.80 0.80 0.80	0.80	Scott-Sanchis
47	0.63 0.63 0.65	0.63	1.00 1.00 0.97	0.99	Megregian-Maier
48	0.83 0.82 0.80	0.82	0.84 0.83 0.82	0.83	Modified ECR
49	0.80 0.86 0.86	0.84	0.80 0.80 0.81	0.80	Megregian-Maier
50	0.80 0.80 0.84	0.81	0.85 0.83 0.83	0.84	Megregian-Maier

COMPARISON OF REPLICATE VALUES

Solution A (0.83 mg/l Fluoride), Distilled

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
SEC	0.78 0.80 0.82	0.80	---- ---- ----	----	None
1	0.80 0.80 0.80	0.80	0.86 0.76 ----	0.81	Megregian-Maier
2	0.66 0.70 0.65	0.67	0.65 0.70 0.55	0.63	Scott-Sanchis
3	0.81 0.76 0.82	0.80	0.79 0.79 0.79	0.79	Scott-Sanchis
4	0.82 0.83 0.83	0.83	0.85 0.92 0.85	0.87	Megregian-Maier
5	0.89 0.81 0.83	0.84	0.90 0.87 0.85	0.87	Megregian-Maier
6	0.77 0.79 0.79	0.79	0.76 0.76 0.76	0.76	Scott-Sanchis
7	0.99 1.00 1.03	1.01	---- ---- ----	----	None
8	0.70 0.72 0.75	0.72	0.70 0.75 0.75	0.73	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
9	0.68 0.66 0.66	0.67	0.86 0.86 0.86	0.86	Megregian-Maier
10	0.80 0.60 0.75	0.72	0.85 0.90 0.80	0.85	Scott-Sanchis
11	0.69 0.64 0.69	0.67	---- ---- ----	----	None
12	0.84 0.82 0.80	0.82	0.80 0.80 0.80	0.80	Scott-Sanchis
13	0.90 0.80 0.90	0.87	0.90 0.90 0.90	0.90	Scott-Sanchis
14	0.86 0.92 0.92	0.90	0.85 0.90 0.80	0.85	Scott-Sanchis
15	0.90 0.86 0.92	0.89	0.84 0.84 0.86	0.85	ECR
16	0.78 0.80 0.78	0.79	0.80 0.80 0.80	0.80	Scott-Sanchis
17	0.85 0.84 0.80	0.83	0.83 0.82 0.81	0.82	Scott-Sanchis

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
18	0.82 0.81 0.83	0.82	0.77 0.80 0.72	0.76	Megregian-Maier
19	0.86 0.84 0.85	0.85	0.90 0.91 0.91	0.91	ECR
20	1.00 1.00 1.04	1.01	1.00 1.00 1.00	1.00	Hellige
21	0.85 0.86 0.85	0.85	0.90 0.90 0.90	0.90	Scott-Sanchis
22	0.78 0.78 0.78	0.78	0.80 0.80 0.80	0.80	Scott-Sanchis
23	0.72 0.72 0.68	0.71	0.80 0.80 0.80	0.80	Scott-Sanchis
24	0.70 0.68 0.65	0.68	0.80 0.90 0.90	0.90	Megregian-Maier
25	0.84 0.82 0.82	0.83	0.79 0.79 0.80	0.79	ECR
26	0.94 0.90 0.94	0.93	0.90 0.90 0.94	0.91	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
27	0.77 0.69 0.72	0.73	0.74 0.74 0.74	0.74	Scott-Sanchis
28	0.80 0.82 0.86	0.83	---- ---- ---	----	None
29	0.89 0.82 0.88	0.86	0.87 0.80 0.86	0.84	Scott-Sanchis
30	1.22 1.07 1.13	1.14	0.45 0.35 0.45	0.42	Megregian-Maier
31	0.90 0.70 0.90	0.83	1.20 0.80 0.70	0.90	Scott-Sanchis
32	0.80 0.80 0.84	0.81	0.79 0.79 0.77	0.78	Megregian-Maier
33	0.96 0.98 0.75	0.90	0.80 0.82 0.80	0.81	Scott-Sanchis
34	0.70 0.75 0.70	0.72	0.75 0.75 0.75	0.75	Scott-Sanchis
35	0.91 0.75 0.66	0.77	0.80 0.75 0.75	0.77	Thorium Nitrate

Lab. No.	SPADNS Replicate Values	SPADNS Average	COMPARATIVE PROCEDURE Replicate Values	COMPARATIVE PROCEDURE Average	Method
36	0.88 0.85 0.87	0.87	0.80 0.84 0.84	0.83	Lamar
37	0.79 0.94 1.03	0.86	0.84 0.84 ----	0.84	Modified SPADNS
38B	0.78 0.80 0.81	0.80	0.76 0.74 0.74	0.75	Scott-Sanchis
39	0.96 0.96 0.96	0.96	0.68 0.64 0.66	0.66	Megregian-Maier
40	0.77 0.77 0.77	0.77	0.73 0.73 0.73	0.73	Thrun
41	0.83 0.83 0.83	0.83	0.80 0.90 0.90	0.87	Scott-Sanchis
42A	0.80 0.80 0.80	0.80	---- ---- ----	----	None
42B	0.80 0.82 0.80	0.80	0.76 0.76 0.82	0.78	SPADNS with steam distillation
42C	0.86 0.86 ----	0.86	0.76 0.76 ----	0.76	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
43	0.85 0.87 0.88	0.86	---- ---- ----	----	None
44	0.21 0.30 0.24	0.25	0.66 0.94 0.78	0.79	Not Identified
45	0.80 0.79 0.79	0.79	0.72 1.04 0.78	0.85	Megregian-Maier
46A	0.80 0.70 0.70	0.73	0.80 0.80 0.80	0.80	Scott-Sanchis
47	0.65 0.65 0.60	0.63	0.74 0.78 0.74	0.75	Megregian-Maier
48	1.04 1.04 1.04	1.04	0.82 0.80 0.84	0.82	Modified ECR
49	0.86 0.86 0.90	0.87	0.87 0.87 0.87	0.87	Megregian-Maier
50	0.86 0.85 0.85	0.85	0.85 0.84 0.82	0.84	Megregian-Maier

COMPARISON OF REPLICATE VALUES

Solution B (0.57 mg/l Fluoride), Undistilled

	SPADNS		COMPARATIVE PROCEDURE		
Lab. No.	Replicate Values	Average	Replicate Values	Average	Method
SEC	0.56 0.59 0.68	0.61	---- ---- ----	----	None
1	0.68 0.57 0.65	0.63	0.10 0.10 0.10	0.10	Megregian-Maier
2	0.55 0.52 0.52	0.53	0.30 0.30 0.20	0.27	Scott-Sanchis
3	0.60 0.54 0.62	0.59	0.27 0.37 0.25	0.30	Scott-Sanchis
4	0.62 0.64 0.64	0.63	0.44 0.45 0.45	0.45	Megregian-Maier
5	0.57 0.55 0.53	0.55	0.35 0.35 0.32	0.34	Megregian-Maier
6	0.57 0.57 0.57	0.57	0.24 0.24 0.24	0.24	Scott-Sanchis
7	1.04 1.08 1.00	1.04	0.75 0.75 0.80	0.77	Hellige
8	0.50 0.50 0.50	0.50	0.10 0.08 0.08	0.09	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
9	0.46 0.44 0.44	0.45	0.36 0.30 0.34	0.33	Megregian-Maier
10	0.50 0.46 0.42	0.46	0.40 0.45 0.45	0.43	Scott-Sanchis
11	0.55 0.48 0.48	0.50	0.50 0.50 0.50	0.50	Megregian-Maier
12	0.64 0.68 0.64	0.65	0.55 ---- ----	0.55	Scott-Sanchis
13	0.50 0.40 0.40	0.40	0.30 0.40 0.40	0.40	Scott-Sanchis
14	0.56 0.48 0.56	0.53	0.45 0.50 0.40	0.45	Scott-Sanchis
15	0.78 0.80 0.91	0.83	0.53 0.52 0.51	0.52	ECR
16	0.66 0.66 0.69	0.67	0.40 0.40 0.40	0.40	Scott-Sanchis
17	0.64 0.61 0.71	0.65	0.40 0.40 0.41	0.40	Scott-Sanchis

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
18	0.63 0.62 0.59	0.61	0.40 0.39 0.41	0.40	Megregian-Maier
19	0.68 0.68 0.68	0.68	0.94 0.88 0.94	0.92	ECR
20	0.80 0.80 0.76	0.79	0.60 0.60 0.60	0.60	Hellige
21	0.66 0.68 0.66	0.67	0.35 0.35 0.35	0.35	Scott-Sanchis
22	0.54 0.54 0.54	0.54	0.44 0.44 0.44	0.44	Scott-Sanchis
23	0.66 0.66 0.66	0.66	0.60 0.60 0.60	0.60	Scott-Sanchis
24	0.63 0.76 0.94	0.78	0.20 0.20 0.20	0.20	Megregian-Maier
25	0.60 0.60 0.64	0.61	0.53 0.53 0.53	0.53	ECR
26	0.48 0.48 0.48	0.48	0.36 0.36 0.36	0.36	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
27	0.49 0.49 0.49	0.49	0.38 0.38 0.38	0.38	Scott-Sanchis
28	0.59 0.61 0.56	0.59	---- ---- ----	----	None
29	0.70 0.58 0.64	0.64	0.22 0.20 0.22	0.21	Scott-Sanchis
30	1.15 0.77 0.77	0.90	0.50 0.68 0.29	0.49	Megregian-Maier
31	0.50 0.60 0.60	0.57	0.60 0.40 0.30	0.43	Scott-Sanchis
32	0.72 0.70 0.71	0.71	0.32 0.32 0.28	0.31	Megregian-Maier
33	0.71 0.62 0.65	0.66	0.28 0.26 0.22	0.25	Scott-Sanchis
34	0.58 0.58 0.62	0.59	0.45 0.43 0.45	0.44	Scott-Sanchis
35	1.15 0.80 0.75	0.90	---- ---- ----	----	None

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
36	0.55 0.58 0.59	0.57	0.24 0.26 0.22	0.24	Lamar
37	0.52 0.56 0.49	0.52	0.48 0.46 0.48	0.48	Modified SPADNS
38B	0.57 0.61 0.62	0.60	0.56 0.59 0.59	0.58	Scott-Sanchis
39	0.63 0.63 0.65	0.64	0.60 0.68 0.66	0.65	Megregian-Maier
40	0.71 0.71 0.71	0.71	0.68 0.68 0.68	0.68	Thrun
41	0.55 0.55 0.59	0.56	0.60 0.60 0.40	0.53	Scott-Sanchis
42A	0.50 0.52 0.48	0.50	---- ---- ----	----	None
42B	0.60 0.70 0.64	0.65	0.54 0.58 0.56	0.56	SPADNS with steam distillation
42C	0.62 0.62 0.62	0.62	0.25 0.26 0.24	0.25	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
43	0.56 0.57 0.56	0.56	---- ---- ----	----	None
44	0.35 0.24 0.27	0.29	0.29 0.37 0.40	0.35	Not Identified
45	0.58 0.59 0.59	0.59	0.08 0.10 0.26	0.15	Megregian-Maier
46A	0.50 0.50 0.50	0.50	0.35 0.35 0.35	0.35	Scott-Sanchis
47	0.44 0.47 0.41	0.44	0.53 0.47 0.55	0.52	Megregian-Maier
48	0.80 0.80 0.81	0.80	0.58 0.60 0.62	0.60	Modified ECR
49	0.48 0.52 0.52	0.51	0.45 0.46 0.43	0.45	Megregian-Maier
50	0.57 0.55 0.58	0.57	0.12 0.11 0.10	0.11	Megregian-Maier

COMPARISON OF REPLICATE VALUES

Solution B (0.57 mg/l Fluoride), Distilled

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
SEC	0.50 0.57 0.57	0.55	---- ---- ----	----	None
1	0.63 0.63 0.63	0.63	0.64 0.64 ----	0.64	Megregian-Maier
2	0.52 0.55 0.55	0.54	0.55 0.55 0.45	0.52	Scott-Sanchis
3	0.58 0.62 0.58	0.59	0.58 0.59 0.57	0.58	Scott-Sanchis
4	0.65 0.64 0.64	0.64	0.56 0.56 0.56	0.56	Megregian-Maier
5	0.57 0.56 0.56	0.56	0.55 0.58 0.58	0.57	Megregian-Maier
6	0.61 0.61 0.61	0.61	0.56 0.56 0.56	0.56	Scott-Sanchis
7	1.00 0.95 0.95	0.97	---- ---- ----	----	None
8	0.50 0.50 0.50	0.50	0.50 0.56 0.52	0.53	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
9	0.36 0.34 0.34	0.35	0.42 0.44 0.42	0.43	Megregian-Maier
10	0.66 0.60 0.60	0.62	0.65 0.60 0.65	0.63	Scott-Sanchis
11	0.49 0.57 0.49	0.52	---- ---- ----	----	None
12	0.56 0.56 0.60	0.57	0.52 ---- ----	0.52	Scott-Sanchis
13	0.40 0.30 0.40	0.40	0.50 0.50 0.50	0.50	Scott-Sanchis
14	0.92 0.92 0.92	0.92	0.60 0.65 0.60	0.62	Scott-Sanchis
15	0.65 0.65 0.67	0.66	0.54 0.55 0.58	0.56	ECR
16	0.67 0.63 0.66	0.65	0.60 0.55 0.60	0.58	Scott-Sanchis
17	0.54 0.55 0.55	0.55	0.58 0.58 0.58	0.58	Scott-Sanchis

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
18	0.62 0.60 0.60	0.61	0.51 0.52 0.50	0.51	Megregian-Maier
19	0.53 0.55 0.53	0.54	0.55 0.54 0.52	0.54	ECR
20	1.10 1.08 1.10	1.09	0.90 1.00 0.90	0.93	Hellige
21	0.66 0.68 0.65	0.66	0.65 0.65 0.65	0.65	Scott-Sanchis
22	0.54 0.54 0.54	0.54	0.56 0.56 0.56	0.56	Scott-Sanchis
23	0.50 0.50 0.50	0.50	0.60 0.60 0.60	0.60	Scott-Sanchis
24	0.42 0.46 0.42	0.43	0.50 0.50 0.50	0.50	Megregian-Maier
25	0.54 0.53 0.50	0.52	0.49 0.50 0.49	0.49	ECR
26	0.68 0.68 0.62	0.66	0.74 0.74 0.72	0.73	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
27	0.70 0.69 0.69	0.69	0.63 0.63 0.63	0.63	Scott-Sanchis
28	0.56 0.59 0.59	0.58	---- ---- ----	----	None
29	0.56 0.57 0.58	0.57	0.60 0.64 0.62	0.62	Scott-Sanchis
30	0.97 0.67 0.68	0.77	0.29 0.35 0.29	0.31	Megregian-Maier
31	0.60 0.50 0.70	0.60	0.60 0.60 0.50	0.57	Scott-Sanchis
32	0.59 0.59 0.59	0.59	0.55 0.55 0.55	0.55	Megregian-Maier
33	0.76 0.79 0.48	0.68	0.64 0.66 0.66	0.65	Scott-Sanchis
34	0.43 0.42 0.44	0.42	0.45 0.45 0.45	0.45	Scott-Sanchis
35	1.08 0.83 0.72	0.88	0.74 0.55 0.61	0.63	Thorium Nitrate

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
36	0.68 0.71 0.70	0.70	0.62 0.60 0.60	0.61	Lamar
37	0.67 0.72 1.04	0.69	0.84 0.73 0.81	0.79	Modified SPADNS
38B	0.44 0.45 0.49	0.46	0.37 0.43 0.40	0.40	Scott-Sanchis
39	0.63 0.63 0.64	0.63	0.46 0.46 0.46	0.46	Megregian-Maier
40	0.46 0.46 0.46	0.46	0.55 0.55 0.55	0.55	Thrun
41	0.60 0.60 0.60	0.60	0.70 0.70 0.70	0.70	Scott-Sanchis
42A	0.58 0.56 0.57	0.57	---- ---- ----	----	None
42B	0.50 0.60 0.58	0.56	0.40 0.44 0.44	0.43	SPADNS with steam distillation
42C	0.57 0.56 ----	0.57	0.53 0.55 ----	0.54	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
43	0.62 0.60 0.65	0.62	---- ---- ----	----	None
44	0.00 0.00 0.00	0.00	0.44 0.52 0.37	0.44	Not Identified
45	0.52 0.53 0.51	0.52	0.62 1.02 0.68	0.77	Megregian-Maier
46A	0.60 0.60 0.60	0.60	0.40 0.40 0.40	0.40	Scott-Sanchis
47	0.36 0.41 0.36	0.38	0.70 0.70 0.66	0.69	Megregian-Maier
48	0.69 0.70 0.70	0.70	0.61 0.61 0.62	0.61	Modified ECR
49	0.72 0.76 0.76	0.75	0.66 0.68 0.68	0.67	Megregian-Maier
50	0.66 0.68 0.68	0.67	0.65 0.65 0.64	0.65	Megregian-Maier

COMPARISON OF REPLICATE VALUES

Solution C (0.68 mg/l Fluoride), Undistilled

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
SEC	0.88 0.91 0.91	0.90	---- ---- ----	----	None
1	0.85 0.85 0.86	0.85	0.80 0.80 0.80	0.80	Megregian-Maier
2	0.92 0.87 0.84	0.88	0.60 0.60 0.50	0.57	Scott-Sanchis
3	0.88 0.86 0.87	0.87	0.61 0.59 0.60	0.60	Scott-Sanchis
4	0.83 0.80 0.80	0.81	0.81 0.78 0.79	0.77	Megregian-Maier
5	0.85 0.84 0.83	0.84	0.60 0.57 0.55	0.57	Megregian-Maier
6	0.83 0.85 0.83	0.84	0.56 0.56 0.56	0.56	Scott-Sanchis
7	1.14 1.16 1.18	1.16	0.90 0.90 0.90	0.90	Hellige
8	0.75 0.72 0.75	0.74	0.81 0.70 0.92	0.81	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
9	0.68 0.68 0.66	0.67	0.40 0.42 0.42	0.41	Megregian-Maier
10	0.74 0.66 0.84	0.75	0.55 0.50 0.55	0.53	Scott-Sanchis
11	0.77 0.79 0.86	0.81	0.70 0.70 0.70	0.70	Megregian-Maier
12	0.80 0.76 0.80	0.79	0.50 0.50 0.50	0.50	Scott-Sanchis
13	0.70 0.70 0.70	0.70	0.50 0.50 0.50	0.50	Scott-Sanchis
14	0.86 0.82 0.86	0.85	0.55 0.60 0.60	0.58	Scott-Sanchis
15	0.98 1.00 0.98	0.99	0.80 0.80 0.78	0.79	ECR
16	0.67 0.70 0.67	0.68	0.55 0.55 0.55	0.55	Scott-Sanchis
17	0.94 0.95 0.88	0.92	0.45 0.47 0.48	0.47	Scott-Sanchis

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
18	0.82 0.82 0.79	0.81	0.61 0.62 0.61	0.61	Megregian-Maier
19	0.80 0.84 0.84	0.83	1.24 1.20 1.20	1.21	ECR
20	0.78 0.82 0.74	0.78	0.60 0.60 0.60	0.60	Hellige
21	0.74 0.74 0.74	0.74	0.55 0.55 0.55	0.55	Scott-Sanchis
22	0.76 0.76 0.76	0.76	0.54 0.54 0.54	0.54	Scott-Sanchis
23	0.82 0.82 0.84	0.83	0.60 0.60 0.60	0.60	Scott-Sanchis
24	0.94 0.79 0.88	0.87	0.50 0.50 0.50	0.50	Megregian-Maier
25	0.90 0.90 0.91	0.90	0.80 0.80 0.80	0.80	ECR
26	0.80 0.80 0.80	0.80	0.75 0.75 0.75	0.75	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
27	0.67 0.67 0.67	0.67	0.43 0.43 0.43	0.43	Scott-Sanchis
28	0.86 0.88 0.82	0.85	--- ---- ----	----	None
29	0.95 0.93 0.93	0.94	0.64 0.70 0.68	0.67	Scott-Sanchis
30	1.67 1.66 ----	1.66	0.50 0.95 0.82	0.76	Megregian-Maier
31	0.90 0.90 ----	0.90	0.60 0.50 0.50	0.53	Scott-Sanchis
32	0.80 0.77 0.80	0.79	0.71 0.65 0.65	0.67	Megregian-Maier
33	0.72 0.74 0.72	0.73	0.48 0.52 0.48	0.49	Scott-Sanchis
34	0.67 0.71 0.70	0.69	0.65 0.63 0.61	0.63	Scott-Sanchis
35	0.76 0.73 0.73	0.74	---- ---- ----	----	None

	SPADNS		COMPARATIVE PROCEDURE		
Lab. No.	Replicate Values	Average	Replicate Values	Average	Method
36	0.87 0.87 0.88	0.87	0.38 0.38 0.36	0.37	Lamar
37	0.62 0.62 0.62	0.62	0.68 0.59 0.62	0.63	Modified SPADNS
38B	0.67 0.67 0.69	0.68	0.63 0.67 0.68	0.66	Scott-Sanchis
39	0.91 0.91 0.91	0.91	0.66 0.72 0.72	0.70	Megregian-Maier
40	0.77 0.77 0.77	0.77	0.69 0.69 0.69	0.69	Thrun
41	0.76 0.78 0.76	0.77	0.60 0.60 0.60	0.60	Scott-Sanchis
42A	0.78 0.81 0.79	0.79	---- ---- ----	----	None
42B	0.86 0.86 0.84	0.85	0.82 0.90 0.86	0.86	SPADNS with steam distillation
42C	0.82 0.83 0.81	0.82	0.30 0.27 0.27	0.28	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
43	0.81 0.82 0.84	0.82	---- ---- ----	----	None
44	0.70 0.74 0.65	0.69	0.62 0.73 0.68	0.68	Not Identified
45	0.82 0.83 0.82	0.82	1.04 0.74 1.00	0.93	Megregian-Maier
46A	0.80 0.80 0.80	0.80	0.55 0.55 0.55	0.55	Scott-Sanchis
47	0.57 0.55 0.55	0.56	1.12 1.01 1.05	1.06	Megregian-Maier
48	1.00 1.02 1.04	1.02	0.78 0.82 0.80	0.80	Modified ECR
49	0.75 0.78 0.82	0.78	0.71 0.60 0.65	0.65	Megregian-Maier
50	0.80 0.81 0.79	0.80	0.82 0.82 0.81	0.82	Megregian-Maier

COMPARISON OF REPLICATE VALUES

Solution C (0.68 mg/l Fluoride), Distilled

	SPADNS		COMPARATIVE PROCEDURE		
Lab. No.	Replicate Values	Average	Replicate Values	Average	Method
SEC	0.64 0.67 0.69	0.67	---- ---- ----	----	None
1	0.68 0.70 0.74	0.71	0.64 0.64 ----	0.64	Megregian-Maier
2	0.62 0.62 0.65	0.63	0.65 0.65 0.55	0.62	Scott-Sanchis
3	0.76 0.71 0.72	0.73	0.68 0.68 0.68	0.68	Scott-Sanchis
4	0.75 0.75 0.75	0.75	0.70 0.71 0.69	0.70	Megregian-Maier
5	0.74 0.71 0.72	0.72	0.75 0.75 0.75	0.75	Megregian-Maier
6	0.65 0.68 0.67	0.67	0.66 0.66 0.66	0.66	Scott-Sanchis
7	1.13 1.10 1.13	1.12	---- ---- ----	----	None
8	0.60 0.60 0.65	0.62	0.67 0.58 0.67	0.64	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
9	0.56 0.54 0.54	0.55	0.58 0.60 0.60	0.59	Megregian-Maier
10	0.75 0.77 0.73	0.75	0.70 0.75 0.65	0.70	Scott-Sanchis
11	0.54 0.52 0.56	0.54	---- ---- ----	----	None
12	0.58 0.66 0.60	0.61	0.65 0.65 0.65	0.65	Scott-Sanchis
13	0.60 0.60 0.70	0.70	0.70 0.70 0.70	0.70	Scott-Sanchis
14	0.92 0.92 0.92	0.92	0.70 0.80 0.70	0.73	Scott-Sanchis
15	0.80 0.77 0.77	0.78	0.71 0.70 0.73	0.71	ECR
16	0.75 0.74 0.73	0.74	0.70 0.70 0.70	0.70	Scott-Sanchis
17	0.74 0.74 0.72	0.73	0.78 0.81 0.79	0.79	Scott-Sanchis

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
18	0.73 0.73 0.73	0.73	0.64 0.68 0.65	0.66	Megregian-Maier
19	0.79 0.84 0.79	0.81	0.80 0.79 0.82	0.80	ECR
20	0.74 0.74 0.74	0.74	1.00 1.00 1.00	1.00	Hellige
21	0.70 0.70 0.69	0.70	0.70 0.70 0.70	0.70	Scott-Sanchis
22	0.68 0.68 0.68	0.68	0.60 0.60 0.60	0.60	Scott-Sanchis
23	0.61 0.62 0.60	0.61	0.60 0.60 0.60	0.60	Scott-Sanchis
24	0.51 0.58 0.70	0.60	0.70 0.70 0.70	0.70	Megregian-Maier
25	0.70 0.71 0.72	0.71	0.73 0.72 0.73	0.73	ECR
26	0.80 0.80 0.80	0.80	0.80 0.80 0.80	0.80	Megregian-Maier

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
27	0.59 0.61 0.56	0.59	0.58 0.58 0.58	0.58	Scott-Sanchis
28	0.74 0.72 0.74	0.73	---- ---- ----	----	None
29	0.77 0.77 0.75	0.76	0.80 0.80 0.80	0.80	Scott-Sanchis
30	1.27 1.27 1.13	1.22	0.29 0.35 0.29	0.31	Megregian-Maier
31	0.70 0.70 0.80	0.73	0.70 0.70 0.60	0.67	Scott-Sanchis
32	0.63 0.63 0.70	0.65	0.67 0.64 0.65	0.65	Megregian-Maier
33	0.83 0.86 0.59	0.76	0.66 0.70 0.70	0.69	Scott-Sanchis
34	0.60 0.70 0.62	0.64	0.65 0.65 0.65	0.65	Scott-Sanchis
35	0.72 0.70 0.70	0.71	0.88 0.63 0.60	0.70	Thorium Nitrate

Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
36	0.72 0.77 0.82	0.77	0.66 0.68 0.68	0.67	Lamar
37	0.79 0.65 0.78	0.74	0.68 0.75 0.77	0.73	Modified SPADNS
38B	0.60 0.63 0.64	0.62	0.59 0.59 0.62	0.60	Scott-Sanchis
39	0.82 0.82 0.82	0.82	0.66 0.64 0.58	0.61	Megregian-Maier
40	0.65 0.65 0.65	0.65	0.67 0.67 0.67	0.67	Thrun
41	0.72 0.73 0.73	0.73	0.80 0.80 0.80	0.80	Scott-Sanchis
42A	0.69 0.71 0.74	0.71	---- ---- ----	----	None
42B	0.70 0.68 0.68	0.69	0.88 0.84 0.88	0.87	SPADNS with steam distillation
42C	0.77 0.77 ----	0.77	0.66 0.68 ----	0.67	Megregian-Maier

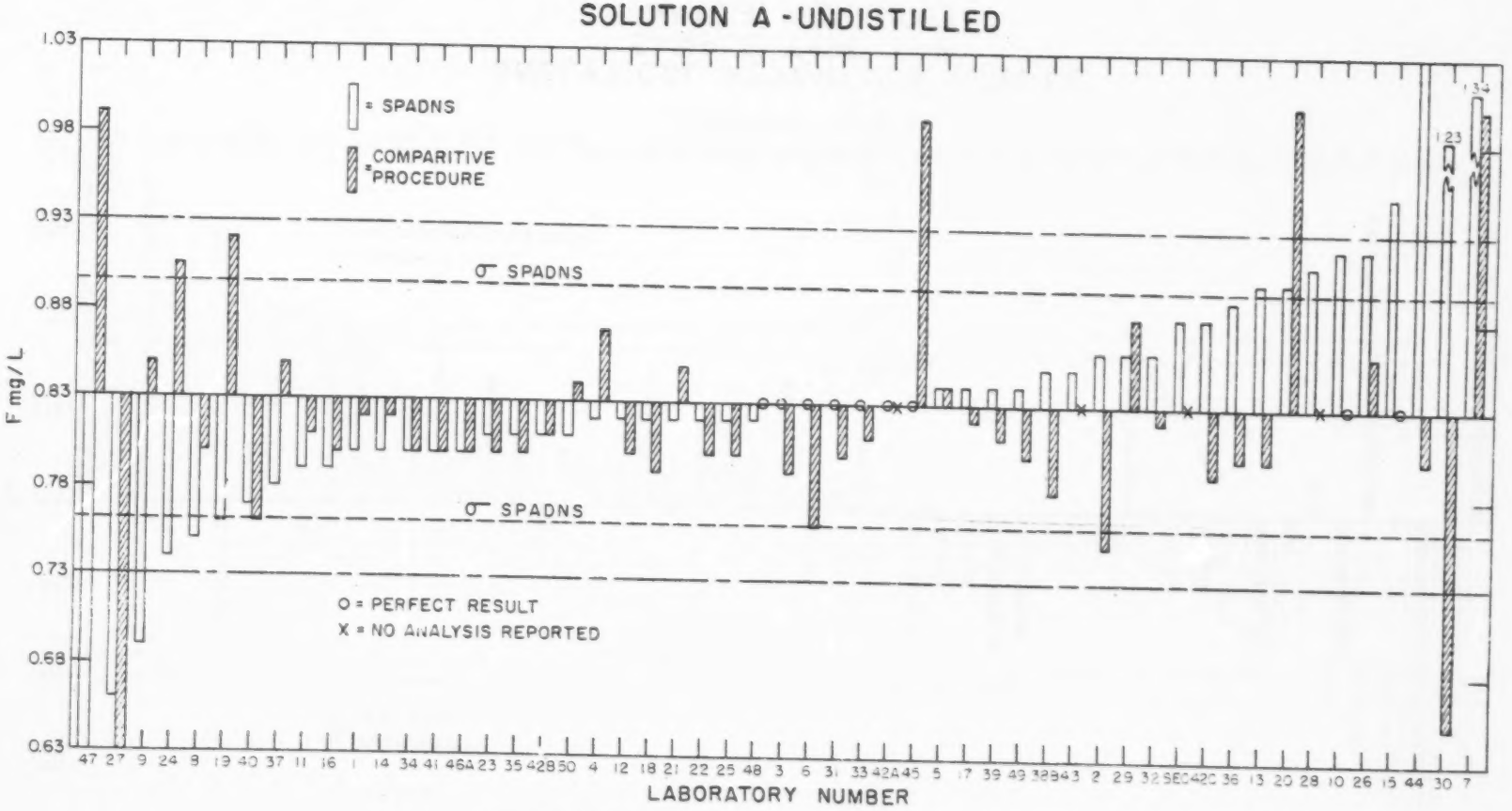
Lab. No.	SPADNS		COMPARATIVE PROCEDURE		
	Replicate Values	Average	Replicate Values	Average	Method
43	0.84 0.81 0.84	0.83	---- ---- ----	----	None
44	0.24 0.24 0.24	0.24	0.20 0.52 0.25	0.32	Not Identified
45	0.67 0.68 0.67	0.67	1.32 1.02 0.56	0.97	Megregian-Maier
46A	0.85 0.60 0.95	0.83	0.55 0.55 0.55	0.55	Scott-Sanchis
47	0.47 0.52 0.52	0.50	0.60 0.74 0.70	0.68	Megregian-Maier
48	0.87 0.88 0.89	0.88	0.81 0.81 0.80	0.81	Modified ECR
49	0.86 0.86 0.86	0.86	0.83 0.83 0.84	0.83	Megregian-Maier
50	0.73 0.73 0.74	0.73	0.70 0.71 0.68	0.70	Megregian-Maier

SUMMARY OF ARITHMETIC MEANS

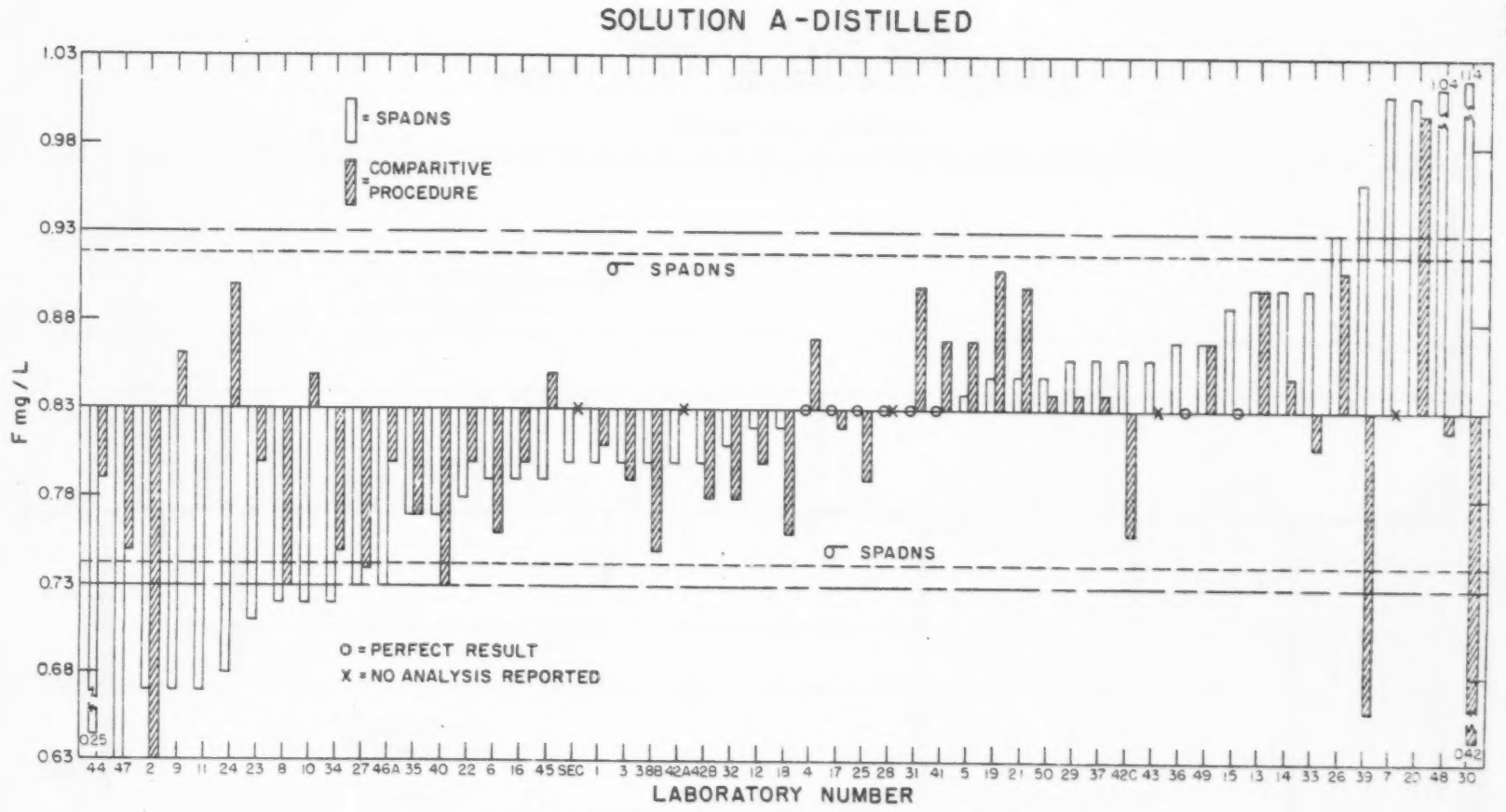
Lab. No.	Solution A - 0.83 mg/l				Solution B - 0.57 mg/l				Solution C - 0.68 mg/l			
	SPADNS		Comparative		SPADNS		Comparative		SPADNS		Comparative	
	Un. Dist.	Dist.	Un. Dist.	Dist.	Un. Dist.	Dist.	Un. Dist.	Dist.	Un. Dist.	Dist.	Un. Dist.	Dist.
SEC	0.88	0.80	----	----	0.61	0.55	----	----	0.90	0.67	----	----
1	0.80	0.80	0.82	0.81	0.63	0.63	0.10	0.64	0.85	0.71	0.80	0.64
2	0.86	0.67	0.75	0.63	0.53	0.54	0.27	0.52	0.88	0.63	0.57	0.62
3	0.83	0.80	0.79	0.79	0.59	0.59	0.30	0.58	0.87	0.73	0.60	0.68
4	0.82	0.83	0.87	0.87	0.63	0.64	0.45	0.56	0.81	0.75	0.77	0.70
5	0.84	0.84	0.84	0.87	0.55	0.56	0.34	0.57	0.84	0.72	0.57	0.75
6	0.83	0.79	0.76	0.76	0.57	0.61	0.24	0.56	0.84	0.67	0.56	0.66
7	1.34	1.01	1.00	----	1.04	0.97	0.77	----	1.16	1.12	0.90	----
8	0.75	0.72	0.80	0.73	0.50	0.50	0.09	0.53	0.74	0.62	0.81	0.64
9	0.69	0.67	0.85	0.86	0.45	0.35	0.33	0.43	0.67	0.55	0.41	0.59
10	0.92	0.72	0.83	0.85	0.46	0.62	0.43	0.63	0.75	0.75	0.53	0.70
11	0.79	0.67	0.81	----	0.50	0.52	0.50	----	0.81	0.54	0.70	----
12	0.82	0.82	0.80	0.80	0.65	0.57	0.55	0.52	0.79	0.61	0.50	0.65
13	0.90	0.87	0.80	0.90	0.40	0.40	0.40	0.50	0.70	0.70	0.50	0.70
14	0.80	0.90	0.82	0.85	0.53	0.92	0.45	0.62	0.85	0.92	0.58	0.73
15	0.95	0.89	0.83	0.83	0.83	0.66	0.52	0.56	0.99	0.78	0.79	0.71
16	0.79	0.79	0.80	0.80	0.67	0.65	0.40	0.58	0.68	0.74	0.55	0.70
17	0.84	0.83	0.82	0.82	0.65	0.55	0.40	0.58	0.92	0.73	0.47	0.79
18	0.82	0.82	0.79	0.76	0.61	0.61	0.40	0.51	0.81	0.73	0.61	0.66
19	0.76	0.85	0.92	0.91	0.68	0.54	0.92	0.54	0.83	0.81	1.21	0.80
20	0.90	1.01	1.00	1.00	0.79	1.09	0.60	0.93	0.78	0.74	0.60	1.00
21	0.82	0.85	0.85	0.90	0.67	0.66	0.35	0.65	0.74	0.70	0.55	0.70
22	0.82	0.78	0.80	0.80	0.54	0.54	0.44	0.56	0.76	0.68	0.54	0.60
23	0.81	0.71	0.80	0.80	0.66	0.50	0.60	0.60	0.83	0.61	0.60	0.60
24	0.74	0.68	0.90	0.90	0.78	0.43	0.20	0.50	0.87	0.60	0.50	0.70

25	0.82	0.83	0.80	0.79	0.61	0.52	0.53	0.49	0.91	0.71	0.80	0.73
26	0.92	0.93	0.86	0.91	0.48	0.66	0.36	0.73	0.80	0.80	0.75	0.80
27	0.66	0.73	0.63	0.74	0.49	0.69	0.38	0.63	0.67	0.59	0.43	0.58
28	0.91	0.83	----	----	0.59	0.58	----	----	0.85	0.73	----	----
29	0.86	0.86	0.88	0.84	0.64	0.57	0.21	0.62	0.94	0.76	0.67	0.80
30	1.23	1.14	0.65	0.42	0.90	0.77	0.49	0.31	1.66	1.22	0.76	0.31
31	0.83	0.83	0.80	0.90	0.57	0.60	0.43	0.57	0.90	0.73	0.53	0.67
32	0.86	0.81	0.82	0.78	0.71	0.59	0.31	0.55	0.79	0.65	0.67	0.65
33	0.83	0.90	0.81	0.81	0.66	0.68	0.25	0.65	0.73	0.76	0.49	0.69
34	0.80	0.72	0.80	0.75	0.59	0.42	0.44	0.45	0.69	0.64	0.63	0.65
35	0.81	0.77	0.80	0.77	0.90	0.88	----	0.63	0.74	0.71	----	0.70
36	0.89	0.87	0.80	0.83	0.67	0.70	0.24	0.61	0.87	0.77	0.37	0.67
37	0.78	0.86	0.85	0.84	0.52	0.69	0.48	0.79	0.62	0.74	0.63	0.73
38B	0.85	0.80	0.78	0.75	0.60	0.46	0.58	0.40	0.68	0.62	0.66	0.60
39	0.84	0.96	0.81	0.66	0.64	0.63	0.65	0.46	0.91	0.82	0.70	0.61
40	0.77	0.77	0.76	0.73	0.71	0.46	0.68	0.55	0.77	0.65	0.69	0.67
41	0.80	0.83	0.80	0.87	0.56	0.60	0.53	0.70	0.77	0.73	0.60	0.80
42A	0.83	0.80	----	----	0.50	0.57	----	----	0.79	0.71	----	----
42B	0.81	0.80	0.81	0.78	0.65	0.56	0.56	0.43	0.85	0.69	0.86	0.87
42C	0.88	0.86	0.79	0.76	0.62	0.57	0.25	0.54	0.82	0.77	0.28	0.67
43	0.85	0.83	----	----	0.56	0.62	----	----	0.82	0.83	----	----
44	1.03	0.25	0.80	0.79	0.29	0.00	0.35	0.44	0.69	0.24	0.68	0.32
45	0.83	0.79	0.99	0.85	0.59	0.52	0.15	0.77	0.82	0.67	0.93	0.97
46A	0.80	0.73	0.80	0.80	0.50	0.60	0.35	0.40	0.80	0.83	0.55	0.55
47	0.63	0.63	0.99	0.75	0.44	0.38	0.52	0.69	0.56	0.50	1.06	0.68
48	0.82	1.04	0.83	0.82	0.80	0.70	0.60	0.61	1.02	0.88	0.80	0.81
49	0.84	0.87	0.80	0.87	0.51	0.75	0.45	0.67	0.78	0.86	0.65	0.83
50	0.81	0.85	0.84	0.84	0.57	0.67	0.11	0.65	0.80	0.73	0.82	0.70

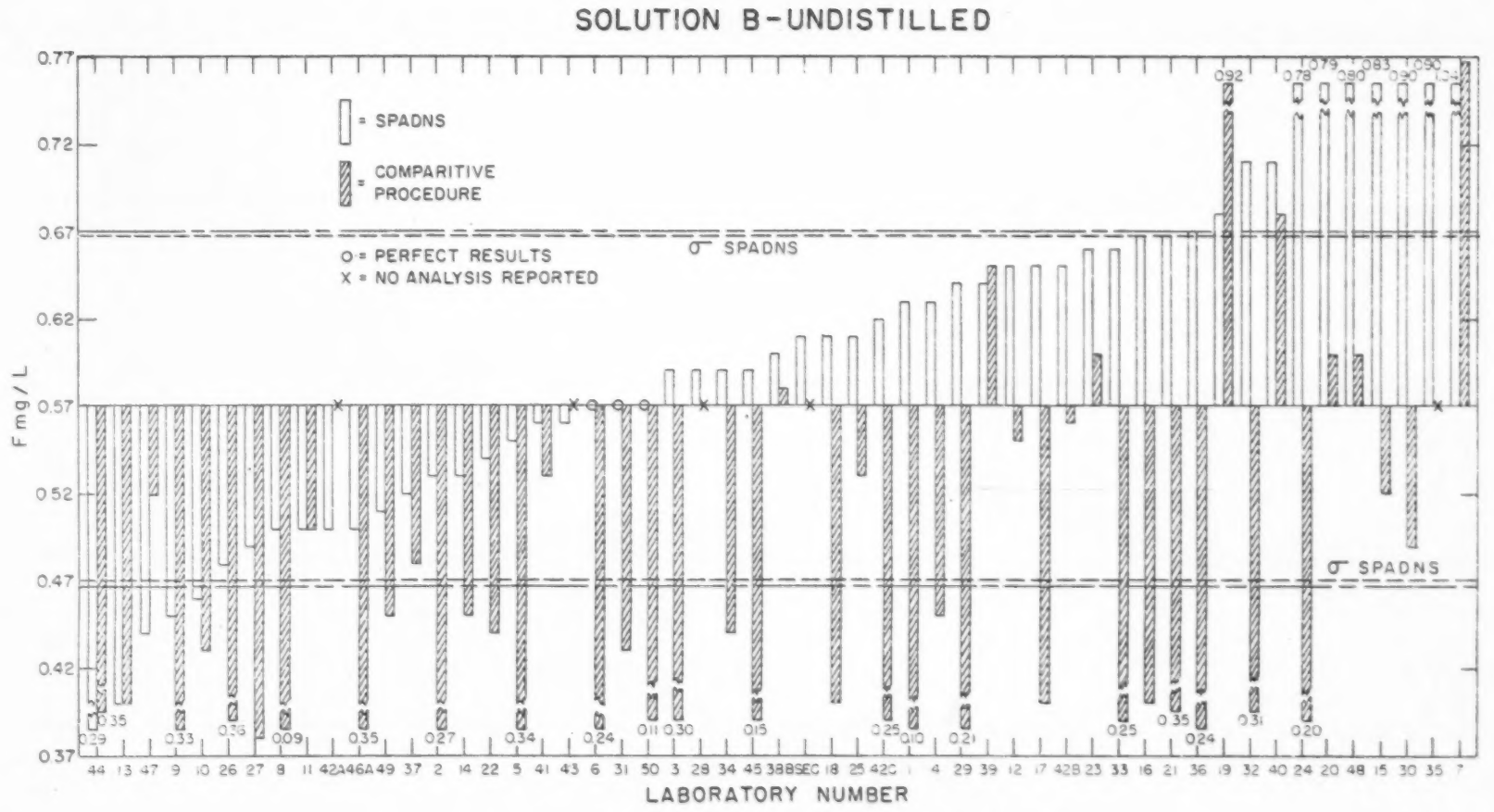
APPENDIX



ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE III-B
(WATER, FLUORIDE)

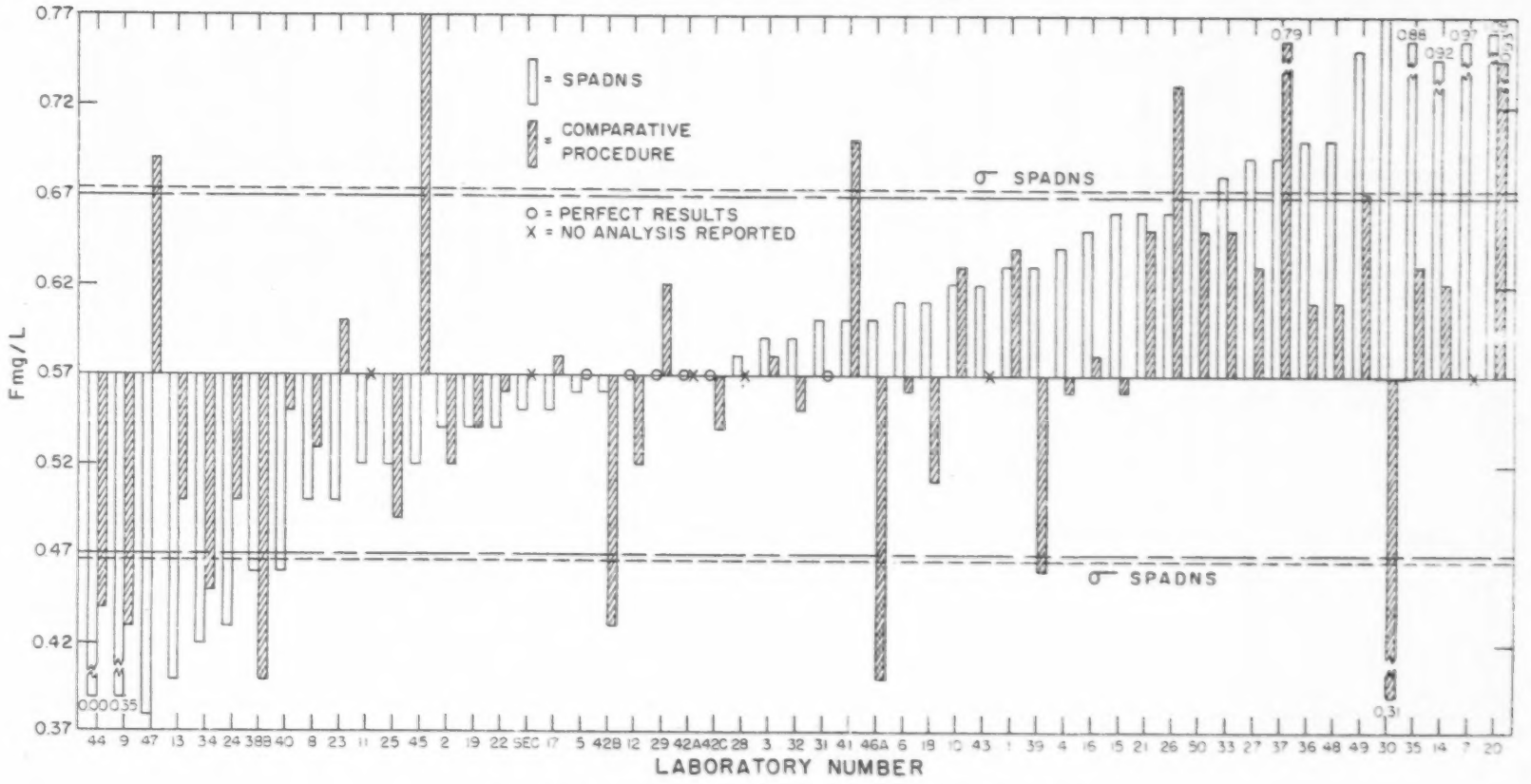


ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE III-B
(WATER, FLUORIDE)



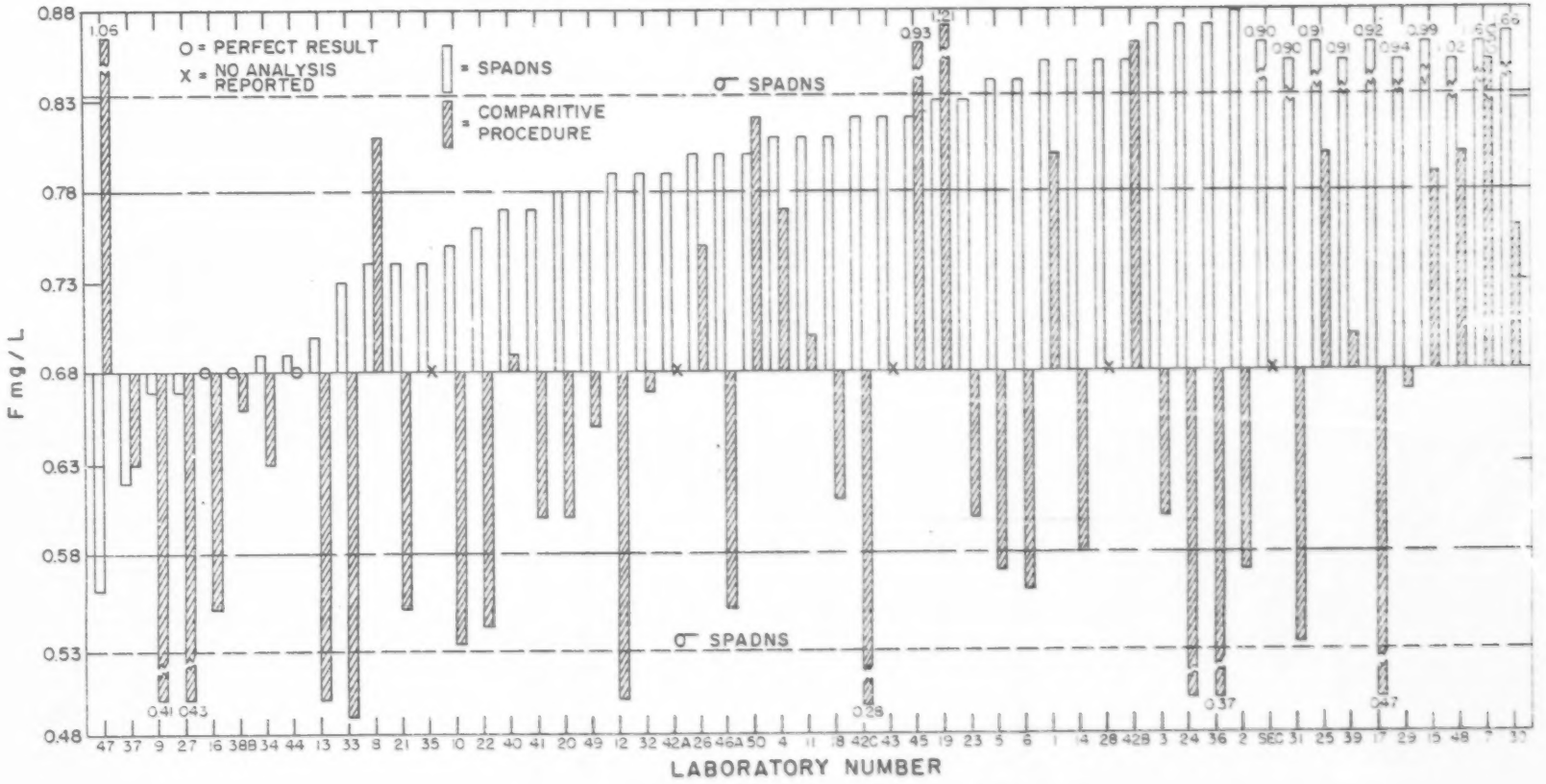
ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE III-B
(WATER, FLUORIDE)

SOLUTION B-DISTILLED

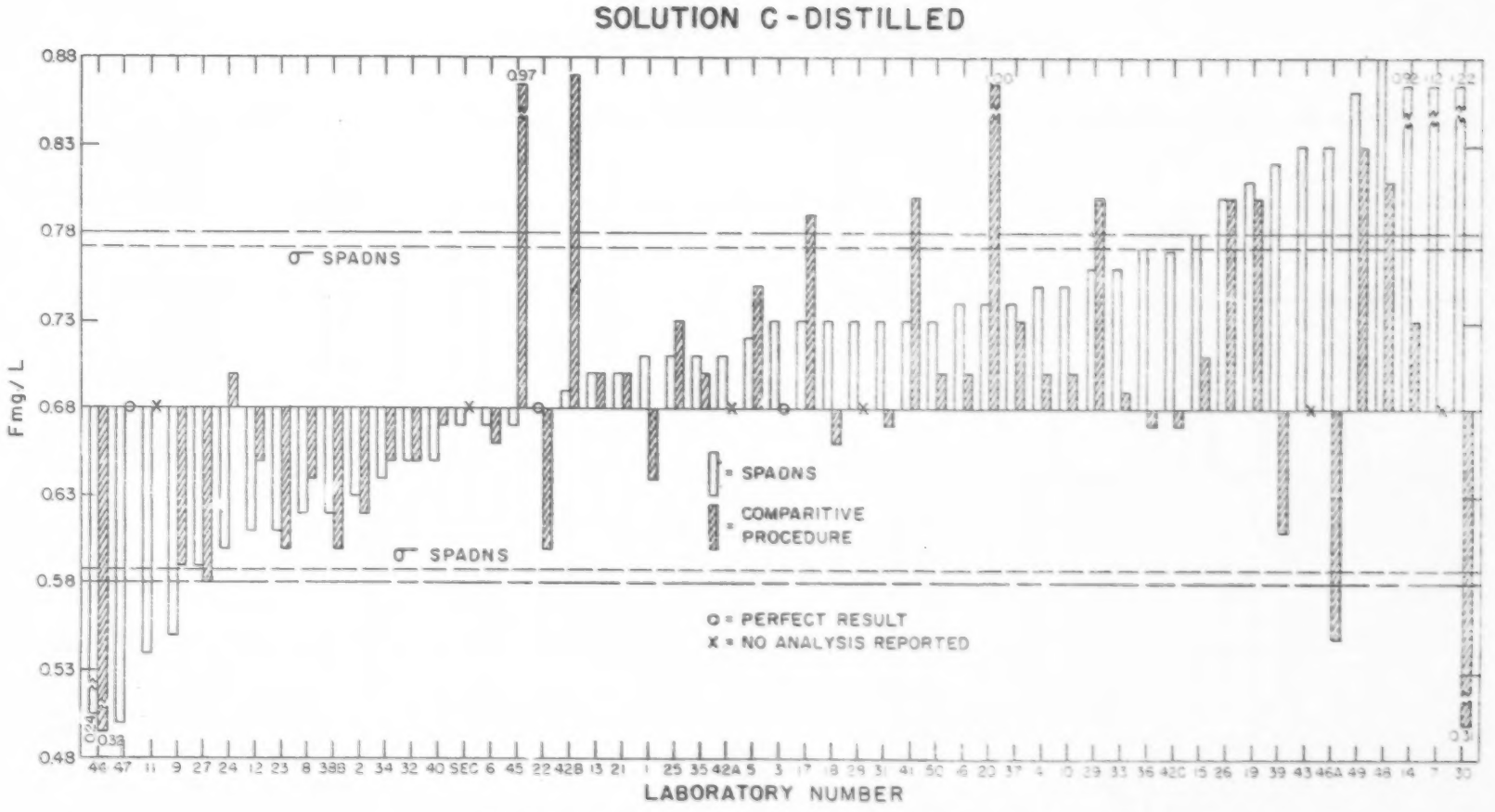


ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE III-B
(WATER, FLUORIDE)

SOLUTION C - UNDISTILLED



ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE III-B
(WATER, FLUORIDE)



ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE III-B
(WATER, FLUORIDE)